SOME STUDIES OF THE REACTION BETWEEN STANNIC CHLORIDE AND SILVER PERCHLORATE IN ANHYDROUS MEDIA

A THESIS

Presented to the University of Cape Town

for the Degree of

Doctor of Philosophy

by

MAX PEISACH, M.Sc.

Department of Chemistry,
University of Cape Town.

August, 1954.

ACKNOWLEDGEMENTS

The author wishes to thank the following:-

(1) Professor W. Pugh and Dr. F. Sebba for the encouragement, guidance and advice given him in the course of his research.

(2) Mr. W.C. Lewis for the time he spent on the construction of the numerous pieces of apparatus that were required.

(3) The other members of the Department of Chemistry of the University of Cape Town for their kind co-operation.

(4) The Council of the University of Cape Town for a grant towards the cost of this research.

CONTENTS

INTRODUCTION

INTRODUCTION

The theory of the chemical bond, particularly in compounds where the bonds are neither purely electrovalent nor purely covalent, has in recent years received a great deal of attention. Of the oxy-acids which can form ionic as well as covalent compounds, perchloric acid and sulphuric acid are of special interest because of the electronic symmetry and the stability of their anions. While compounds of the elements of group IV, in the divalent state, are known to be ionic, the exact nature of the bonds formed by these elements in the tetravalent state in their oxy-salts has as yet not been ascertained. It would, therefore, be of interest to review the perchlorates and sulphates of that group.

Group IVa - Titanium.

Numerous sulphates of titanium both in the trivalent and tetravalent states are known. A sulphate of divalent titanium, $TiSO_4$, has been reported[1] but its existence has since been questioned[2].

Hydrated tetravalent titanium sulphates of the form $Ti(SO_4)_2,nH_2O$ have been crystallised with three[6], four[7] and nine[8] molecules of water, but the only way in which anhydrous titanic sulphate has been prepared in a

crystalline/...

crystalline form, is by reaction of titanic chloride and sulphur trioxide in sulphuryl chloride[5], according to the reaction

$$TiCl_4 + 6SO_3 \longrightarrow Ti(SO_4)_2 + 2S_2O_5Cl_2$$

Whereas the preparation of simple titanic sulphate requires carefully controlled conditions, acid and basic sulphates are much easier to obtain. Thus, the acid salt, $2TiO_2,3SO_3,3H_2O$, crystallises from a solution of titanium oxide in sulphuric acid at 120°C. Above 225°C. this solution yields crystals of the basic salt $TiOSO_4$[9]. Another acid salt easily prepared is $Ti(SO_4)_2,H_2SO_4,4H_2O$, which can be obtained by decomposing nitrous titanium compounds with 50% sulphuric acid[3].

In addition to the basic titanyl sulphate, $TiOSO_4$, already referred to, and its hydrated forms containing one[10], two[9] and five[11] molecules of water, other salts with widely differing ratios of titanic oxide to sulphur trioxide to water have been prepared.

Ionic titanium sulphates with the titanium atom in the anion occur in two forms, $Ti(SO_4)_3^{--}$[11] or $OTi(SO_4)_2^{--}$[12]. Because these sulphato-titanates contain 6-covalent titanium they fall outside the scope of this review.

Titanyl perchlorate, $TiO(ClO_4)_2nH_2O$ is the only titanium perchlorate that has been prepared[13]. It was

obtained/...

obtained by fuming titanic chloride with perchloric acid. The resulting solution was concentrated in vacuo until colourless hexagonal plates crystallised. When this salt was treated with an equimolecular quantity of hydrogen peroxide and then dehydrated in vacuo over phosphorus pentoxide for several days, it yielded a peroxide addition compound, $TiO(ClO_4)_2,H_2O_2$[13]. Both the original salt and its peroxide complex were very easily hydrolysed.

Zirconium.

Since the lower valency states of zirconium are much less stable than those of titanium, only simple compounds of di- and trivalent zirconium have been prepared, namely, the chlorides[14], the bromides[15] and the iodides[16].

The simple anhydrous sulphate, $Zr(SO_4)_2$, can be obtained as a white powder when zirconium dioxide or zirconyl chloride is fumed with concentrated sulphuric acid, but the product always contains excess sulphuric acid[17]. When the sulphate thus formed is dissolved in dilute sulphuric acid, hydrated zirconium sulphate crystallises. The product, though corresponding to a formula of $Zr(SO_4)_2,4H_2O$ is considered to be $H_2[O{=}Zr(SO_4)_2]3H_2O$ since, on electrolysis, the zirconium migrates to the anode[18]. Its proposed structure is similar to that of one of the sulphato-titanate anions.

Various/...

Various acid salts crystallise from a solution of zirconium sulphate in which the sulphur trioxide content exceeds 64%. Thus, between 64 and 72% sulphur trioxide $Zr(SO_4)_2,H_2SO_4,2H_2O$ is obtained as well-defined crystals; with 72 to 79% sulphur trioxide, fine crystals of $Zr(SO_4)_2,H_2SO_4,H_2O$ can be obtained, but when the sulphur trioxide exceeds 79% an amorphous powder of indefinite composition approximating to $Zr(SO_4)_2,H_2SO_4$ settles out[19].

Basic zirconium sulphates can be obtained from dilute aqueous solutions. When kept at 40°C. a basic salt, $7ZrO_2,5SO_3,30\ H_2O$, forms as fine needles. Dialysis of the sulphate solution yields a basic salt $2ZrO_2,SO_3,7H_2O$[19]. Sulphato-zirconates of the form $K_4[Zr(SO_4)_4]nH_2O$ and $(NH_4)_2[Zr(SO_4)_3]3H_2O$ are relatively well-established salts, whose structures compare with the corresponding sulphato-titanates.

The perchlorates of zirconium which have been reported are:-

(i) $ZrO(ClO_4)_2$, which is obtained by dissolving freshly precipitated zirconium hydroxide in dilute perchloric acid[20],

(ii) $ZrO(OH)_2,9ZrO(ClO_4)_2$, which is soluble in alcohol, ether and benzene, but which is decomposed by water[21], and

(iii)/...

(iii) $4ZrO(ClO_4)_2HClO_4$, which is water soluble and, as it is not easily hydrolysed, can be crystallised from aqueous solution.

Hafnium.

The marked similarity between the chemistry of hafnium and zirconium is largely due to the similarity in size of both the atom (1.48Å) and the ion (0.87Å). Hafnium, however, is somewhat more basic than zirconium. Raman spectra have shown that in aqueous solution the hafnyl ion, $HfO_2^{\cdot\cdot}$ forms very readily[22].

Anhydrous hafnium sulphate, $Hf(SO_4)_2$, can be prepared by heating hafnium compounds to fumes with concentrated sulphuric acid[23] but the compound formed is invariably contaminated by excess acid[24]. When the solution is treated with sulphuric acid, the solubility of the salt decreases, but when the sulphur trioxide content exceeds 60% the solubility increases owing to the formation of $H_2[Hf(SO_4)_3]$ or $H_2[HfO(SO_4)_2]$[25]. Use is made of the increased solubility of hafnium in concentrated sulphuric acid to effect separation from zirconium. From solutions of hafnium sulphate, $Hf(SO_4)_2 4H_2O$ may be formed[26]. When the solution is left to stand, a basic salt $4HfO_2, 3SO_3 14H_2O$ forms[25].

No perchlorate compound of hafnium has been reported.

Thorium/...

Thorium.

Thorium, the most basic of the group IV elements, forms simple ionic salts of which the sulphate, $Th(SO_4)_2$, is a typical example. From aqueous solutions various hydrates containing two, four, six, eight and nine molecules of water may be crystallised[27]. It is remarkable that the sulphate requires a long period of time to establish equilibrium between the crystalline and dissolved states. This probably accounts for the fact that the hydrates $(Th(SO_4)_2 6H_2O$ and $Th(SO_4)_2 8H_2O$ can readily be crystallised even though they are both metastable for all ranges of temperature.

Double sulphates, sulphato-thorates, of the form $M_2[Th(SO_4)_3]$ can be obtained with rubidium, caesium and sodium, while potassium and ammonium form the double sulphates $M_4[Th(SO_4)_4]$[28,29].

The only thorium perchlorate that has been prepared is $Th(ClO_4)_4 nH_2O$. Cleve[30] claims to have obtained this hydrate, of unknown composition, in the form of an hygroscopic solid.

Group IVb - Carbon.

The simplest sulphato compounds of carbon are the sulphonic acids, which are substituted derivatives of

sulphuric/...

sulphuric acid, and the sulphates, which are esters of organic alcohols. It is quite clear that these compounds differ basically from the inorganic type of salt usually referred to as "sulphates" and the inclusion of these organic compounds in a review of this kind is out of place.

While a similar argument holds for most of the perchloro compounds, the preparation of a perchloro compound from carbon tetrachloride is of special interest because the procedure that was used might be applicable to the preparation of perchlorates of the other group IV elements.

Trichloromethyl perchlorate, CCl_3ClO_4, was prepared from anhydrous carbon tetrachloride by reaction with anhydrous silver perchlorate in the presence of a small trace of hydrogen chloride as catalyst[31]. The product was obtained by fractional distillation in vacuo at -80°C. and was found to be a colourless, freely mobile liquid solidifying at -55°C. Though stable at low temperatures, the liquid was found to decompose slowly at room temperature and explosively at higher temperatures. The presence of organic matter such as tap greases and solvents caused explosive decomposition, but cold solutions in carbon tetrachloride were stable. Because of the danger of explosion, the separation of trichloromethyl perchlorate from carbon tetrachloride was not carried to completion, about 5 - 10% carbon tetrachloride remaining.

The/...

The analysis of the trichloromethyl perchlorate gave very unsatisfactory results. These results (table 1) show a marked deviation from those expected for a pure compound, even when undistilled carbon tetrachloride is allowed for.

Table 1

Composition of trichloromethyl perchlorate

(From the paper by Birckenbach and Goubeau[31])

	C	Cl	O
Theoretical	5.51%	65.11%	29.38%
Experimental	5.01%	67.06%	27.78%

The high chlorine and low oxygen values are consistent with the presence of 5 - 7% of free carbon tetrachloride as suggested by the authors. A contradiction arises, however, in the case of the carbon content. The low experimental value cannot be explained by the presence of carbon tetrachloride, since any unreacted material would raise the carbon content above the theoretical value. The authors tentatively suggested the formation of a diperchloro compound, $CCl_2(ClO_4)_2$, but pointed out as well that the presence of such a compound would lead to a higher instead of a lower oxygen content. Consequently, there is some doubt as to the exact nature of their product.

Silicon/...

Silicon.

No sulphate or perchlorate of silicon has been reported.

Germanium.

Although two series of germanium compounds exist in which the germanium atom can be divalent or tetravalent, no sulphate or perchlorate of divalent germanium has been prepared.

The dissociation constant of germanic acid was found by Pugh to be slightly higher than that of silicic acid[32], but the solubility of germanium dioxide in sulphuric acid decreased with increasing concentration of acid. Even in 16N sulphuric acid (95%) the solubility was only 1.4 g. per litre. It was therefore shown that germanic sulphate could not be formed in aqueous solution. Under anhydrous conditions Schwartz[33] prepared a sulphate, $Ge(SO_4)_2GeO_2$, by treating germanium tetrachloride with sulphur trioxide. The product was, however, easily hydrolysed to germanium dioxide.

After having failed to prepare germanium perchlorate from germanium dioxide and perchloric acid, Østerud and Prytz[34] attempted to obtain this compound by reaction between equivalent quantities of germanium tetrachloride and

silver/...

silver perchlorate. Germanium chloride was added to a solution of silver perchlorate in concentrated perchloric acid, but after the silver chloride precipitate had been filtered off, the filtrate gave no test for germanium. A similar result was obtained when the silver perchlorate was dissolved in ethyl alcohol instead of concentrated perchloric acid. It was concluded that the germanium had been removed with the silver chloride and that no germanium perchlorate had been prepared.

A further attempt at preparing the perchlorate was made by heating concentrated perchloric acid and germanium tetrachloride for several hours in a sealed tube at 190°C.(34). After 3 - 4 hours at this temperature a white coating, which contained germanium, had formed in the tube. When the tubes were cut open a gas that smelt of chlorine escaped. The residual yellow liquid was left to crystallise and yielded rhombic crystals which, when dissolved in perchloric acid, gave spot tests for germanium. Since hypochlorites and chlorites are unstable and since chlorates usually form monoclinic crystals, the authors claimed that they had prepared germanium perchlorate. The low yield was attributed to "the small tendency (of germanium) to form polar bindings".

The insufficiency of the claim made by Østerud and Prytz is obvious. Not only were no analyses carried out,

but/...

but the theoretical explanation offered is vague. It is clear that the authors expected an ionic perchlorate but since there is no theoretical reason why germanium perchlorate should be ionic, their explanation for the low yield is valueless. If, on the contrary, germanium perchlorate were covalent, the low yield could most easily be explained by their use of polar, instead of non-polar, solvents, the presence of which could have interfered with the formation of a covalent compound. Their claim to have prepared germanium perchlorate, based, as it is, only on crystalline form, cannot be considered conclusive.

Tin.

Both series of tin salts, the divalent stannous series and the tetravalent stannic series, are more easily prepared and are more stable than the corresponding salts of germanium.

Stannic sulphate, $Sn(SO_4)_2 2H_2O$, and the dihydroxy salt $Sn(OH)_2SO_4$ have been crystallised[36,37]. X-ray powder diagrams of the former have been made, but the exact structure of the salt has not been worked out.

When freshly precipitated stannic oxide is dissolved in dilute sulphuric acid, the dihydrate can be obtained as colourless needles[35], the composition of which

agrees/...

agrees with the above formulation. Despite this evidence, Sidgwick[38] claims that the sulphate exists as a solution of stannic hydroxide in sulphuric acid, but cannot be isolated. It would appear that this author interprets the composition of stannic sulphate and its corresponding dihydroxy derivative as $SnO_2,2H_2SO_4$ and SnO_2,H_2SO_4 respectively. Before any finality on this controversial point can be arrived at, more X-ray evidence will be required.

In their studies of the polarographic reduction of tin, Østerud and Prytz[39] required a solution of stannic perchlorate. Since there was no previous reference to this compound, they had to devise their own synthesis. A solution of stannic chloride, acidified with dilute perchloric acid, was treated with the exact equivalent of silver perchlorate. When the silver chloride was filtered off, the filtrate was suitable for their purpose. Without further experimentation and without any attempt at isolating the product, these authors claimed that they had prepared stannic perchlorate, which they formulated as $Sn(ClO_4)_4$. In effect, however, all that Østerud and Prytz were investigating was a solution containing equivalent concentrations of perchlorate ions and stannic tin, so that their claim to have synthesized stannic perchlorate is completely unfounded.

Apart from the article mentioned above, there is

no/...

no reference to a perchlorate of tetravalent tin. It must therefore be concluded that no stannic perchlorate has as yet been prepared.

Lead.

The most common lead salts are the divalent plumbous and the tetravalent plumbic compounds. While an apparently monovalent sulphate, lead subsulphate, Pb_2SO_4, has been reported[40], it is doubtful whether the "monovalent" form was free from other lead impurities. Under such circumstances its composition must be open to doubt.

Plumbic sulphate, $Pb(SO_4)_2$, was reported by Brauner in 1894[46]. The easiest way to prepare this salt was by the electrolysis of about 80% sulphuric acid between lead electrodes. Using a current density of 2 - 6 amps per square decimeter the electrolysis was allowed to proceed for a considerable time at 30°C. and finally for several hours at 50°C. When the solution was cooled, a yellowish crystalline powder, $Pb(SO_4)_2$, separated. A colourless basic sulphate, $Pb(OH)_2SO_4$, usually formed as an intermediate and could be isolated.

Plumbous perchlorate solutions may be obtained by dissolving metallic lead in dilute perchloric acid[42]. The hydrated lead perchlorate, which is obtained as white

needles/...

needles from a solution of lead oxide in perchloric acid, can be formulated as $Pb(ClO_4)_2 3H_2O$[43,44]. A basic perchlorate, $Pb(ClO_4)_2 PbO, 2H_2O$, has also been reported[45]. No perchlorate of tetravalent lead has as yet been prepared.

Summary.

From the above review the following points emerge:

(1) Though many basic and complex sulphates of the elements of group IVa have been prepared, the simplest sulphates of the form $M^{IV}(SO_4)_2$ require special conditions for their preparation.

(2) Except in the case of thorium, the sulphates, $M^{IV}(SO_4)_2$ are formed under conditions more favourable to the formation of covalent than ionic compounds.

(3) In the tetravalent state, the metals do not form simple ions. The exceptions are thorium and lead. Evidence for the existence of $Th^{\cdot\cdot\cdot\cdot}$ abounds, while the presence of $Pb^{\cdot\cdot\cdot\cdot}$ ions has been proved by the exchange of radioactive and inactive lead in acetic acid solutions of plumbic acetate. It had previously been shown that exchange in non-ionised plumbic compounds did not take place[47]. Raman spectra of solutions of titanium, zirconium and hafnium sulphate suggest the ion $[M^{IV}O]^{\cdot\cdot}$, while stannic ions are probably hydrated. Ionic

germanic/...

germanic compounds containing the ion Ge^{++++} do not exist.

(4) The chemistry of the sulphates is considerably better known than that of the perchlorates.

(5) Where perchlorates have been prepared, the salts are invariably complex.

(6) In order to prepare perchlorates of group IV, conditions favouring the formation of covalent rather than ionic compounds should be chosen.

Scope of the work.

In view of the above conclusions, drawn from the comparative chemistry of the sulphates of the elements of group IV, and, to a lesser extent, their perchlorates it was decided to investigate the possible synthesis of the perchlorates of which so much less is known. The tetrachlorides of the elements of group IVb have typical covalent properties and are soluble in a large number of organic solvents. The chloride could thus be used as starting material. As a source of the perchlorate radical, two possibilities exist, namely, anhydrous perchloric acid and anhydrous silver perchlorate. It was deemed inadvisable

to/...

to use anhydrous perchloric acid, because not only the acid itself, but also its solutions in ether[45] and benzene[48] are explosive; on the other hand, solutions of silver perchlorate in ether and benzene are stable[49,50] and can be used to prepare other perchlorates under anhydrous conditions. Work was consequently begun in an attempt to prepare the tetraperchlorates of the elements of group IV.

Owing to the instability of covalent perchlorate compounds, it was decided to start the investigation with the more polar element - tin - in preference to silicon or germanium. The availability of stannic chloride and the explosive nature of lead tetrachloride[47] were additional factors influencing the choice of starting point.

Throughout this investigation, moisture had to be completely excluded. The presence of even traces of moisture interfered with the reaction and very serious errors were observed when quantitative measurements were taken. As a result, special procedures had to be developed for the preparation of the driest stannic chloride, while the silver perchlorate had to be dehydrated by a tedious procedure of prolonged heating at controlled temperatures and under the lowest possible pressures. Furthermore, the experiments had to be carried out in closed systems which had been carefully dried beforehand. Whenever

aliquots/...

aliquots of anhydrous solutions had to be drawn, elaborate precautions had to be taken to exclude atmospheric moisture, so that even simple operations became tasks requiring the utmost care.

Apart from the danger of contamination by moisture, the experimental work was accompanied by a certain amount of personal risk. On several occasions explosions occurred for no apparent reason. Consequently most of the experiments had to be conducted with small quantities of material and behind explosion screens, which hampered the operator and added to the difficulties of developing the necessary techniques. While the use of explosion screens lessened the danger of personal injury, such danger was not completely excluded, since certain operations, like weighing, could not conveniently be carried out behind screens.

The development of the necessary techniques left no time for the investigation of the reaction between silver perchlorate and the chlorides of the other elements of group IV. Consequently only the case of stannic chloride was dealt with.

The preparation of the reagents is described in Section A. Silver perchlorate was prepared from silver carbonate and perchloric acid by a method very similar to

that/...

that used by Hill[50]. Anhydrous stannic chloride, commercial grade, was available and this was purified by a modification of the distillation method used by Kabesh and Nyholm[52]. The purity of both reagents was confirmed by analysis.

Before proceeding with the main investigation, attempts were made to prepare stannic perchlorate from stannic oxide and perchloric acid. These attempts showed that hydrated stannic oxide was peptized to form an unstable sol in perchloric acid, but that no stannic perchlorate formed. This work is described in the first part of Section B.

The remainder of Section B deals with the preliminary investigations of the reaction between silver perchlorate and stannic chloride in ether and in benzene. In both these solvents, the results indicated that some reaction did take place, but more refined techniques were necessary to isolate and identify the main product. During the trial reaction in ether, the formation of the stannic chloride-ether complex, $SnCl_4, 2(C_2H_5)_2O$, was confirmed. The ease with which perchlorates explode was demonstrated by an explosion which occurred in the trial reaction in benzene. This emphasized the need for caution in later experiments, which were accordingly carried out with small quantities of materials.

Section C/...

Section C deals with the investigation of the reaction in benzene. In the introductory part of this section, Part 1, it was proved that under completely anhydrous conditions a precipitate of silver chloride formed when stannic chloride was added to a benzene solution of silver perchlorate. When centrifugation was used to separate the precipitate, the presence of a second liquid phase, black or dark brown in colour, was revealed. The elucidation of the composition of this liquid phase is discussed in Part 2 and forms the major part of this section. The investigations of the supernatant benzene phase, which contained unreacted stannic chloride or silver perchlorate, and the precipitate, consisting almost entirely of silver chloride, are described in Part 3. Although evidence was obtained for the formation of organic compounds, these could not be isolated or identified.

Analysis of the black liquid phase showed that its composition varied with the conditions under which it was prepared. It was found that when excess silver perchlorate was used in its preparation, the black liquid probably consisted of stannic perchlorate, benzene and unreacted silver perchlorate, but when excess stannic chloride was used, the black liquid phase probably contained stannic perchlorate, benzene, perchloric acid and unreacted stannic

chloride/...

chloride. The presence of free perchloric acid was inferred from analytical results and corroborated by the value of the refractive index of redistilled samples. It was considered likely that the explosive nature of the liquid was largely due to the presence of mixtures of anhydrous perchloric acid and benzene[48]. Attempts to purify the black liquid and to separate the stannic perchlorate proved unsuccessful.

As a result of the failure of the direct approach, attempts were made to infer the nature of the main reaction products from the quantities of the reagents used in the reaction. This work is discussed in Part 4. A series of experiments showed that the "reaction ratio", i.e. the number of moles of silver perchlorate that reacted per mole of stannic chloride, varied with the "initial ratio", i.e. the number of moles of silver perchlorate added per mole of stannic chloride, but it was deduced that for stochiometric quantities, initial ratio = 4, the main products were stannic perchlorate and silver chloride. Perchloric acid, found only when the initial ratio was less than 4, was probably formed by a side reaction involving benzene. All the results of the reaction in benzene are summarised in Part 5.

Section D deals with the investigation of the reaction between stannic chloride and silver perchlorate in

ether/...

ether. As the preliminary investigation showed that silver perchlorate was quantitatively converted to silver chloride, an apparatus was assembled to investigate the reaction and to separate the tin compound formed. In addition, attempts were made to separate the silver chloride quantitatively. The investigation showed that stannic perchlorate was probably the main reaction product and that subsequently reaction with ether led to decomposition and the formation of free perchloric acid.

As the presence of solvents complicated the over-all reaction, it was decided to investigate the heterogeneous reaction between stannic chloride vapour and solid silver perchlorate. This investigation is reported in Section E. Stannic chloride vapour was distilled through a plug of solid silver perchlorate, whereupon it was found that reaction took place on the surface of the solid. The volatile materials were separated and fractionated with a small temperature difference between the distillation and receiver bulbs. This technique led to the isolation of small samples of pure stannic perchlorate as easily volatile, colourless needle-like crystals. The composition of the crystals was confirmed by analysis.

For/...

For the sake of continuity, Section F, dealing with the analytical procedures used during the investigation, is relegated to the end. Silver and tin were usually analysed by the sulphide method, but, for the micro-determination of tin, a polarographic method was used. Perchlorates were determined by reduction with titanous sulphate and chlorides by the Volhard titration method.

A microdiffusion method for the determination of perchlorate was developed, similar to that used for the determination of chloride. Although certain difficulties in the procedure remain to be solved, the method could be relied upon to give results with an accuracy of better than 2%.

SECTION A

PREPARATION OF THE REAGENTS

PREPARATION OF THE REAGENTS

The preparation of silver perchlorate.

Anhydrous silver perchlorate was prepared by a method very similar to that used by Hill[50]. A solution of 60% perchloric acid, free from chloride and sulphate, and diluted with distilled water was neutralized with excess silver carbonate. The undissolved silver carbonate was filtered off and the solution was evaporated to dryness.

The crude silver perchlorate was dissolved in water and decomposed with a slight excess of sodium hydroxide solution. The precipitated silver oxide was thoroughly washed to remove alkali and perchlorates and after having been dried at 110°C., it was dissolved in perchloric acid. A slight deficiency of acid was used to ensure complete absence of free acid in the final product. The undissolved silver oxide was filtered off and the solution was concentrated by evaporation until crystallisation started. The crystals were filtered off and dried by heating in a water-bath at 100°C. under a reduced pressure of 15 mm. until most of the moisture had been removed. It was necessary to keep the salt at a temperature above 43°C. to decompose the hydrate, $AgClO_4,H_2O$[51]. The pressure was reduced to 0.1 mm. and heating was continued for several hours. Final

dehydration/...

dehydration was achieved by heating, in vacuo, in a glycerol bath at 120°C. for 15 hours.

The pure silver perchlorate formed the stock from which samples were drawn as required. Each sample was then stored in a vacuum desiccator over phosphorus pentoxide for several days and analysed before use. The substance is exceedingly hygroscopic, but when proper precautions were taken to exclude moisture during the weighing of the sample, the preparation was shown by analysis to be pure.

Different methods of analysis were used to check the purity of the silver perchlorate. The methods used are given in Section F and the results obtained are tabulated in table 15, pages 139 and 140.

The preparation of stannic chloride.

The stannic chloride that was available was anhydrous, commercial grade, as supplied by the British Drug Houses. It contained hydrogen chloride and moisture as impurities.

The removal of the hydrogen chloride presented no difficulty. At -80°C. hydrogen chloride is still gaseous, while stannic chloride is a solid with a low vapour pressure. When a sample of stannic chloride was cooled in a mixture of dry ice and alcohol to -80°C., the gaseous hydrogen chloride

could/...

could be pumped off, leaving the stannic chloride free from this contaminant.

The moisture could not be removed in as simple a manner. For the early investigations it was sufficient to distil about two-thirds of the sample of stannic chloride, the residual third, which contained the moisture, being discarded. In later experiments, when it was essential to use only the driest product, the last traces of moisture were removed by a modification of the method used by Kabesh and Nyholm[52].

The apparatus used is shown in figure 1. Stannic chloride was introduced into bulb A and, after a relatively large amount of phosphorus pentoxide had been added, the wide neck at the top of the bulb was sealed off. After the hydrogen chloride had been removed by pumping at -80°C., the bulb was evacuated through B to 10^{-5} mm. pressure and sealed off. The mixture was then heated at 100°C. for several hours, during which time the moisture was fixed by the phosphorus pentoxide. Heating the closed system was not dangerous, since at this temperature the vapour pressure of stannic chloride is only some 600 mm. After two days the sealed tube was again heated. When the contents had cooled the stannic chloride was ready for distillation.

The rest of the apparatus (figure 1) was connected

to/...

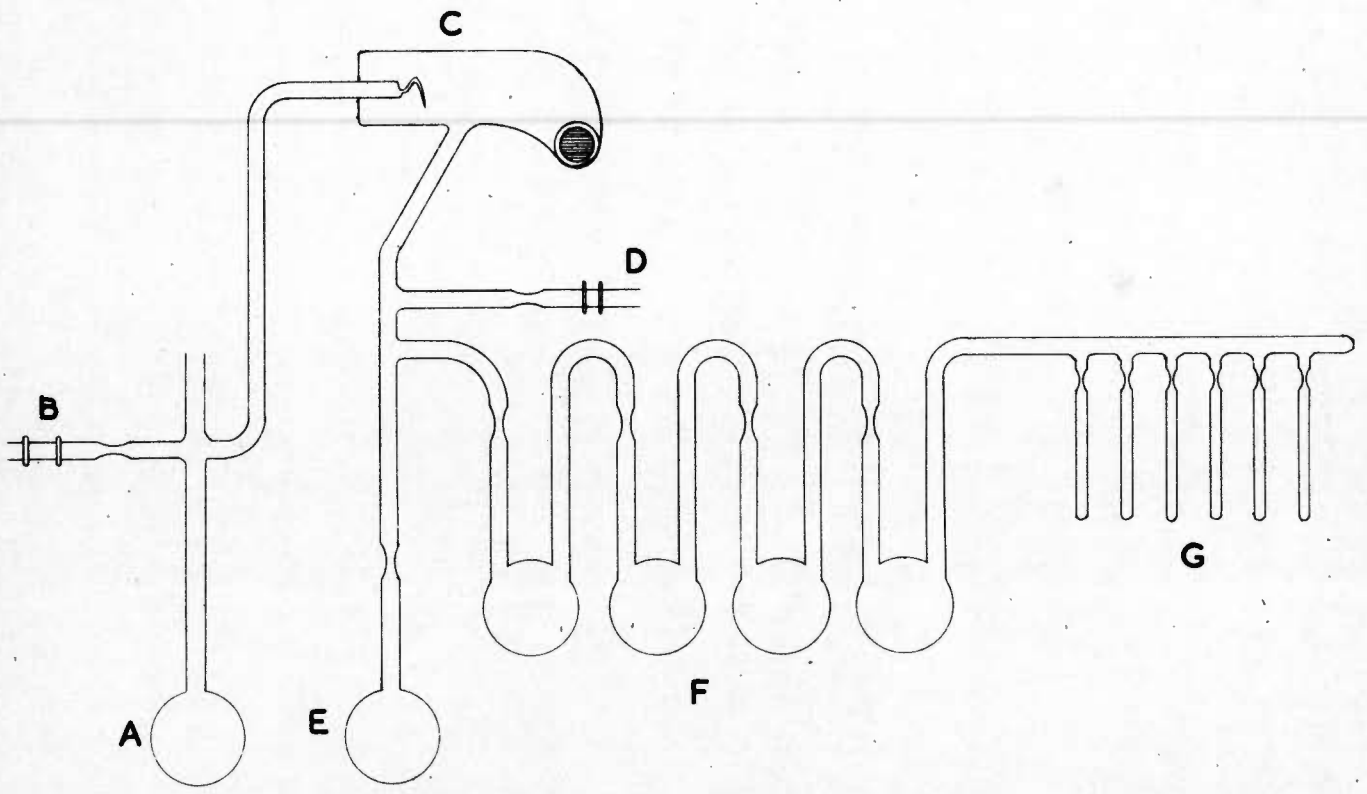


FIGURE 1

to bulb A through a capillary seal, C, which could be broken by a steel ball, controlled magnetically.

The apparatus was evacuated to 5×10^{-6} mm. pressure and sealed off at the constriction at D. With bulb E cooled in a liquid air bath the capillary, C, was broken by the steel ball, while A was kept at about $-10^{\circ}C$. The distillation from A to E was allowed to proceed for only two minutes, during which time the more volatile materials including last traces of hydrogen chloride as well as some stannic chloride condensed in E. This fraction was sealed off and discarded. The liquid air bath was transferred to the first of the bulbs, F, and, when about 80% of the stannic chloride from A had distilled, the bulb was sealed off at the constriction.

About two-thirds of the liquid was distilled into the second bulb, after which the first bulb was sealed off. The process was repeated from the second to the third, and from the third to the fourth bulb, which contained the purest stannic chloride and from which about 1 c.c. was distilled into each of the capillary tubes, G. The capillary tubes were sealed off and stored for future use. The sample collected in the last capillary, which was most likely to contain impurities was used for analysis. The analytical methods are described in Section F and the results are tabulated in table 16, page 141.

SECTION B

PRELIMINARY INVESTIGATIONS

PRELIMINARY INVESTIGATIONS

Trial reaction between stannic oxide and perchloric acid.

The absence of references to stannic perchlorate seemed to indicate that the preparation of this compound could not be carried out by the simple reaction between stannic oxide and aqueous perchloric acid. It was decided, however, to investigate this reaction qualitatively before proceeding with the investigation of the reaction between stannic chloride and silver perchlorate.

Freshly precipitated stannic oxide appeared to dissolve in excess aqueous perchloric acid. The resulting colloidal solution was carefully evaporated but no crystalline product was obtained. A sample of the acid solution, which was left to stand overnight, yielded a white precipitate, presumably hydrated stannic oxide, containing no perchlorate.

Although freshly precipitated stannic oxide appeared to dissolve in dilute perchloric acid, ageing reduced the solubility. Samples left to dry overnight were found to be only slightly soluble, while ignited stannic oxide did not dissolve at all. Even after the acid suspension had been heated for a long time, no tin could be found in the filtered solution. The concentration of perchloric acid appeared to have no effect on the results.

This/...

This behaviour of stannic oxide towards perchloric acid is very much the same as that towards nitric and sulphuric acids. When freshly precipitated with ammonia, stannic oxide is in the form of α-stannic acid, which, on drying or heating, changes to the β-form. Since the former is acid soluble and the latter insoluble, the apparent solubility of stannic oxide will depend on the relative concentration of α-stannic acid.

Mecklenburgh[74,75,76] showed α- and β-stannic acid to be colloidal substances differing only in the size of their particles. More recent investigations have confirmed this point of view. From light diffraction studies, Menon[73] concluded that the particle size of α-stannic acid was approximately the wave-length of light while the particles of the β-acid were larger. The X-ray diffraction patterns obtained by Weiser and Milligan[82] proved that the two forms of stannic acid were structurally identical but contained more or less adsorbed water. It thus appeared that the process of dissolving α-stannic acid was merely peptisation. This point of view was supported by the general behaviour of the "solutions" of stannic oxide in perchloric acid.

Since stannic compounds in aqueous solutions hydrolyse to form stannic oxide, and since stannic oxide

does/...

does not form the perchlorate in perchloric acid, it was concluded that stannic perchlorate could not be prepared by this method.

Trial reaction between stannic chloride and silver perchlorate in ether.

To a solution of silver perchlorate in ether a few drops of commercial anhydrous stannic chloride were added. A precipitate - of silver chloride - formed at once. When the ether solution was concentrated by evaporation, however, no crystalline product was obtained; instead it left a small yield of gummy black residue which was insoluble in nitric acid.

Because failure might have been the result of hydrolysis, a fresh solution of silver perchlorate was prepared in anhydrous ether. The silver content of an aliquot part of this solution was determined. Known weights of stannic chloride were added to samples of the silver perchlorate solution from a stoppered weighing bottle. Reaction took place immediately. The mixture became yellowish, and on standing, deposited a creamy coloured precipitate. This was filtered off and dried at 120°C. Its weight, however, was greater than the maximum possible weight of silver chloride, which indicated that some other

compound/...

crystals were completely volatile at 120°C., the high yield of precipitate obtained earlier could not have been caused by the presence of this substance nor by any impurity in the ether.

Table 2

Analysis of stannic chloride-ether complex

% Sn	% Cl	% Ether (by difference)	Mol. Ratio Sn : Cl : $(C_2H_5)_2O$
28.1	33.6	38.3	1.00 : 4.00 : 2.18
28.2	33.6	38.2	1.00 : 3.99 : 2.17
28.2	33.6	38.2	1.00 : 3.99 : 2.17
28.2	33.5	38.3	1.00 : 3.98 : 2.18
28.1	33.5	38.3	1.00 : 4.00 : 2.18

Another sample of the precipitate obtained from the reaction between ethereal solutions of the dry reagents - silver perchlorate and stannic chloride - was washed with anhydrous ether and then suspended in water. The suspension was made ammoniacal to dissolve silver chloride, and filtered. The clear solution was acidified with chloride-free nitric acid and boiled to coagulate the reprecipitated silver chloride. The precipitate was filtered, washed with ammonium nitrate and nitric acid,

dried/...

dried at 120°C. and weighed. It was found that, although conversion of silver perchlorate to silver chloride was complete, the silver chloride did not account for the whole weight of the precipitate.

When the reaction in ether was more thoroughly investigated (see Section D, pp. 91 - 99) it was found that the weight of precipitate formed under the conditions of these preliminary experiments had little significance. The decomposition of the main product of the reaction, stannic perchlorate, would produce perchloric acid and probably some organic compounds, all of which would add to the weight of the precipitate. It was, however, sufficient that the preliminary experiment had shown that the reaction produced an, as yet, unknown compound in the reaction products.

Trial reaction of silver perchlorate and stannic chloride in benzene.

Indications of reaction in ether encouraged the search for other possible solvents. As a result of the thorough investigation of the benzene/silver perchlorate system made by Hill[51], and the miscibility of stannic chloride and benzene, it was decided to investigate the reaction in this solvent.

Because/...

Because thiophene, which is always present in commercial benzene, is known to be polymerized by stannic chloride[91], it was removed by the method of Ardagh and Furber[77]. In later work 'analar' benzene, as supplied by the British Drug Houses, was available. This benzene was free from most impurities and only required drying before use.

Since mixtures of benzene and perchloric acid are explosive[48], and since the reaction mechanism suggested for the preparation of trichloromethyl perchlorate[78] postulated the formation of perchloric acid, it was considered advisable to use small quantities in trial experiments. Accordingly, about 0.1 g. anhydrous silver perchlorate was dissolved in about 100 c.c. dry benzene, and to the clear solution a large excess of stannic chloride was added. It was doubtful whether any reaction took place, as the precipitate which formed may have been due to hydrolysis. Consequently the reaction mixture was distilled to recover the thiophene-free benzene. When most of the benzene had been removed, the temperature rose rapidly until at 112°C. a few drops of residual black mixture boiled and exploded violently. This behaviour was analogous to that of covalent perchlorates and suggested that some unstable perchlorate had been formed. The more

detailed/...

detailed investigation of the reaction is discussed in the next section.

The explosion showed that it was essential to exercise extreme caution in later experiments. While the cause of the above detonation was the application of heat, this was not the case in two other explosions that occurred during later work (see pages 58 and 62). The former of these explosions occurred while a sample of distillate was in a weighing bottle and the latter, just at the beginning of an attempted microfractionation, when the temperature was about 40°C. The explosions could not be accounted for by any cause common to all three.

As it appeared that the material under investigation could detonate at any time, it was necessary to take all possible precautions at every stage of the research. For this reason the experiments were carried out on small quantities of materials. Safety screens, leather gloves and face masks were used, but these frequently hindered the manipulation of small amounts of reagents. To overcome these difficulties many of the experiments were carried out in vacuum systems, which could easily be screened from the operator, and were suitable for handling small quantities of materials. A further advantage of vacuum apparatus was that moisture could be excluded from the reaction mixture.

SECTION C

REACTION IN BENZENE

REACTION IN BENZENE

PART 1

INTRODUCTORY

Description of the apparatus.

Part of a vacuum fractionating apparatus, shown in figure 2, was available. The apparatus consisted of three fractionation bulbs (A) connected to the main vacuum line and to each other. The pressure in each bulb could be measured independently by manometers (B). A three-way tap (C) connected the fractionating portion to the pumping system, which was protected by traps (D). The pumping system consisted of an electrically operated mercury vapour diffusion pump (E) and a Hyvac oil backing pump (F). The backing pump could, when operated alone, reduce the pressure to below 0.1 mm. The mercury vapour pump was normally closed off from the rest of the system, but by using taps on either side of it, could be connected into the circuit when required.

There were three points of entry into the apparatus. By using standard Quickfit ground glass joints, pieces of apparatus could be connected at G. Gases could be

introduced/...

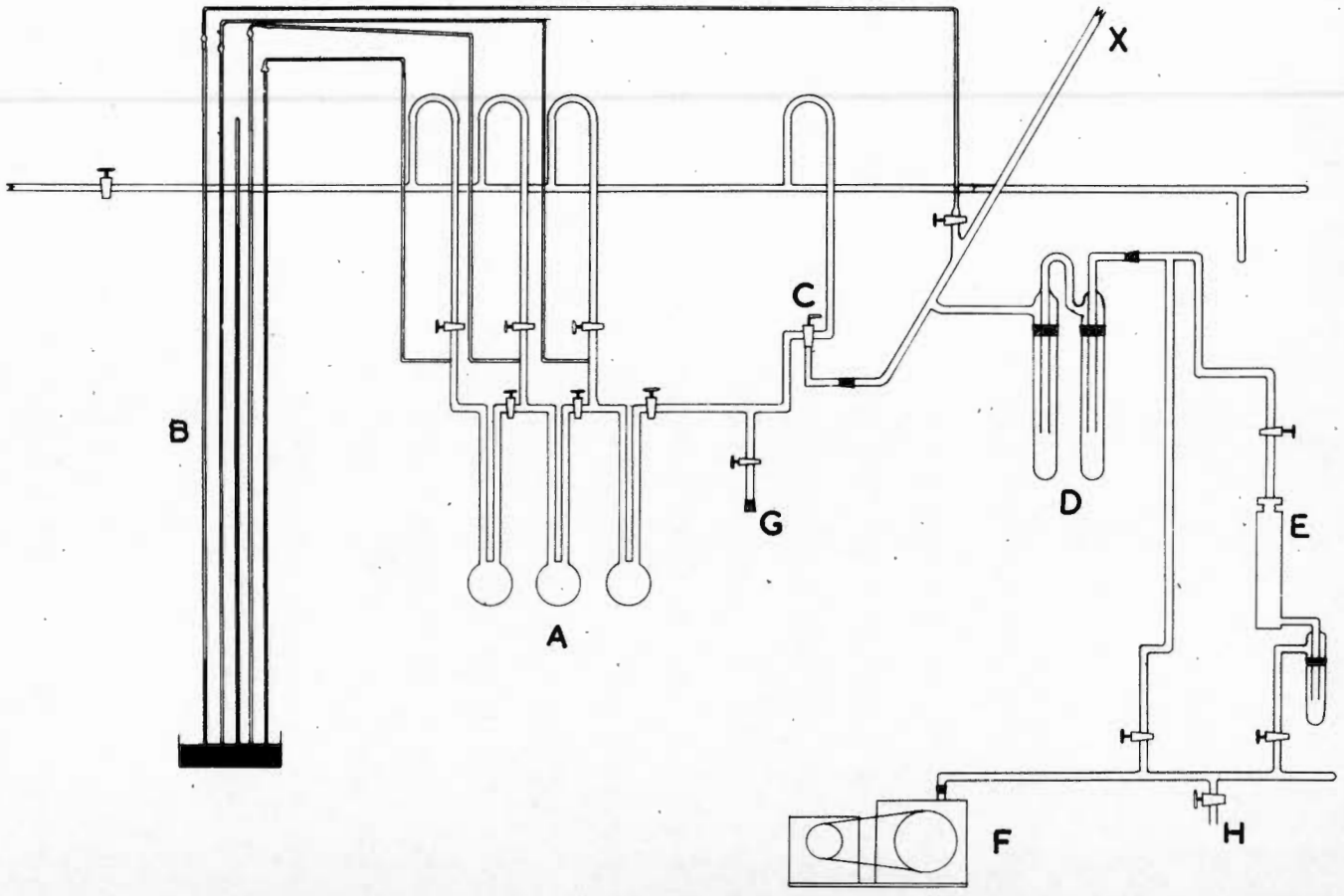


FIGURE 2

introduced through H. The latter point of entry was used to break the vacuum, when air, dried by passing through U-tubes of calcium chloride and a column of phosphorus pentoxide, was allowed to flow in. The third point of entry was at X, where other vacuum systems could be sealed onto the apparatus when these were required.

Only the pumps and traps of this apparatus were used. The fractionation bulbs were found to be of little use because of the rapid deterioration of the grease in contact with vapours of stannic chloride and benzene. Whenever fractionation was necessary it was carried out in a separate all-glass apparatus.

A simple vacuum apparatus, figure 3, consisting of a series of differently sized test tubes connected to each other in series and to the main line in parallel, was sealed onto the main vacuum system at X. The two points of entry into this apparatus were standard ground glass joints, a cone at M and a socket at N, to which other pieces of apparatus could be connected. Each test tube could on its own serve as a point of entry. When the combined apparatus had been thoroughly evacuated and flamed to remove adsorbed moisture, a few drops of stannic chloride were introduced through M. It was found that the presence of stannic chloride vapour affected the lubricant at the taps,

and/...

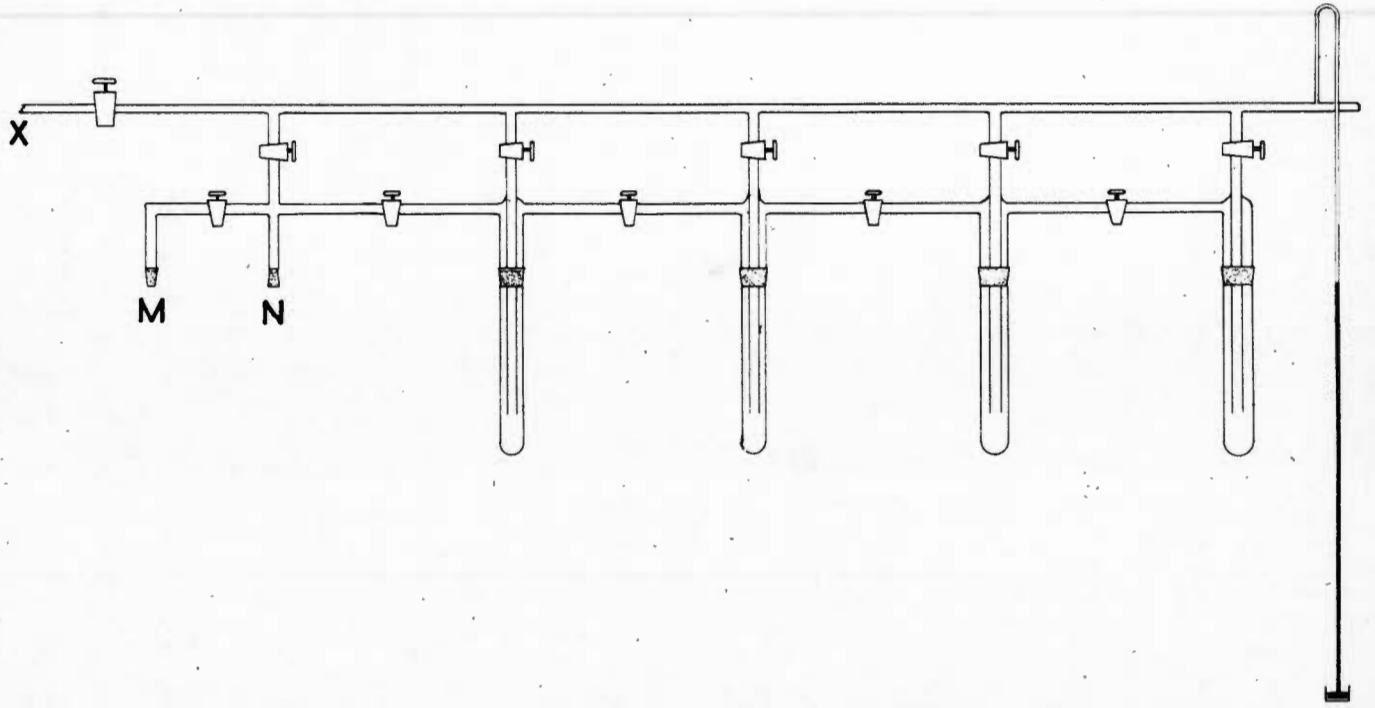


FIGURE 3

and allowed leaks to develop after, at most, eight hours. Because of the action of stannic chloride it was necessary to complete any experiment within this period since, after that time, the seepage of air into the apparatus would introduce sufficient moisture to give misleading results, and the increased pressure would slow down the distillation rate of any material that had to be distilled.

Trial reaction in vacuum system.

A trial reaction between stannic chloride and silver perchlorate was carried out in the apparatus described in the previous paragraph. After silver perchlorate had been weighed into one of the test tubes of the vacuum apparatus (figure 3) the salt was thoroughly dehydrated by heating it under low pressure for several hours in a glycerol bath at 120°C. About 100 c.c. anhydrous thiophene-free benzene were distilled into another test tube and redistilled onto the anhydrous silver perchlorate. The mixture in the apparatus was gently rocked until all the salt had dissolved.

Stannic chloride was poured into a separate test tube fitted with a tap, and connected at N. Though hydrolysis, producing hydrogen chloride, might have taken place when the liquid was poured into the test tube, the

former/...

former would most certainly have been removed when the tube, cooled to -80°C., was evacuated. The tube was then filled with dry air and weighed. It was reconnected to the vacuum apparatus, some stannic chloride was distilled into another part of the apparatus for later use, the tube was again filled with dry air, disconnected and reweighed. The loss of weight corresponded to the weight of stannic chloride introduced into the apparatus.

The stannic chloride was transferred into the solution of silver perchlorate in benzene by distillation, but this operation required the receiver tube to be cooled. The disadvantage of this procedure was that, on being cooled, silver perchlorate crystallised from the benzene solution and did not redissolve when the mixture was left to warm up to room temperature. Any interaction between stannic chloride and silver perchlorate in such a heterogeneous system would have had to take place on the surface of the silver salt and would have been slower than in a simple homogeneous solution in benzene. In addition, as silver chloride, which would form in the reaction, would deposit on the solid and greatly reduce its effective surface, this procedure would be expected to give a low yield of product.

A few experiments in which the stannic chloride was distilled into the benzene solution of silver perchlorate

were/...

were carried out. The reaction mixture was allowed to stand for about an hour, after which all volatile materials were pumped off. The residue consisted mainly of unreacted silver perchlorate but also contained a small amount of gummy black material which, at the time, was assumed to be traces of grease, and some silver chloride. The weight of silver chloride showed that less than 1% of the available silver perchlorate had reacted in each experiment.

To avoid the crystallisation of silver perchlorate and in so doing prevent the formation of a heterogeneous system, it was decided to introduce the stannic chloride without distillation. To this end a clear solution of silver perchlorate in benzene was prepared in one of the tubes of the apparatus, and anhydrous stannic chloride was distilled into an adjacent tube. The tube containing the silver perchlorate solution was connected to the main vacuum line and, with the oil pump working, the tap connecting the tubes containing the stannic chloride and the benzene solution was carefully opened. This drove a current of stannic chloride vapour into the solution. A white precipitate formed immediately. Since the current of stannic chloride through the tap forced small quantities of grease into the reaction mixture, and since some benzene and stannic chloride were removed by the action of the pump, it

was/...

was impossible to obtain quantitative results. The formation of the precipitate, which contained appreciable amounts of silver chloride, did, however, show that under anhydrous conditions a reaction between stannic chloride and silver perchlorate took place.

The next problem was to separate the precipitate without exposure to atmospheric moisture. As a possible solution it was decided to centrifuge the mixture. The reaction had therefore to be carried out in a centrifuge tube by a modified technique.

Anhydrous silver perchlorate was weighed into a dry test tube, small enough to fit into a centrifuge. The tube was connected at M (figure 3) and heated at 120°C. under low pressure for about an hour to remove absorbed moisture. About 100 c.c. anhydrous benzene, dried over phosphorus pentoxide were distilled into the test tube. After the tube had been filled with dry air, it was disconnected and quickly stoppered. The mixture was vigorously shaken to dissolve all the silver perchlorate and gave a clear solution. Other similar solutions were prepared in the same way. It was observed that moisture, even in relatively small quantities, gave cloudy solutions. Whenever a cloudy solution was obtained, it was discarded.

Small quantities of anhydrous stannic chloride

were/...

were weighed directly into each solution, using a Lunge-Reys pipette for the purpose. The stoppers were immediately replaced to avoid unnecessary contamination by atmospheric moisture. In each case a white precipitate formed immediately but did not settle very quickly. The stoppered tubes were transferred to a centrifuge and centrifuged at 3000 - 3500 r.p.m. for about 3 - 5 minutes. When the tubes were removed the contents were found to be made up of three phases viz:-

(i) a lower solid phase consisting of almost pure silver chloride,

(ii) an upper, clear liquid phase, consisting of a solution of unchanged stannic chloride in benzene, and

(iii) an intermediate brown liquid phase clearly separated from the benzene phase. The boundary between the solid phase and this liquid phase was so diffuse that complete separation was impossible. The elucidation of the composition of this liquid phase formed the major part of the investigations.

A delivery tube, protected from atmospheric moisture was introduced into the test tube and the benzene solution was sucked off. The residual mixture of brown liquid and solid material was washed several times with anhydrous benzene. After each wash the colour of the

liquid/...

liquid became more intense until, after the seventh wash, it appeared completely black. When washing was stopped, after the seventh wash, the wash liquid was still found to contain stannic chloride. After a final centrifugation the black liquid was removed in the same way as was the benzene phase.

In this way pure samples were obtained of each of the three phases present in the original reaction mixture. The investigations of each phase are discussed under the appropriate headings in Parts 2 and 3 (pages 43 and 70).

PART 2

THE EXAMINATION OF THE BLACK LIQUID PHASE

Only a very little black liquid was prepared in the trial reaction, but that experiment indicated a convenient method by which it could be prepared. Because of the danger of detonation, small quantities of black liquid were prepared and used as required. At no time was any considerable amount kept in reserve.

Analytical investigation.

(a) Qualitative analysis.

The sample of black liquid that was prepared in the trial reaction was used for qualitative analysis, the results of which showed that the material contained tin, silver, chloride and perchlorate.

When some of the black liquid was poured into water, it appeared to hydrolyse immediately, producing a grey solid which dissolved in aqueous ammonia and reprecipitated on being acidified with nitric acid. One of the products of hydrolysis was therefore silver chloride. The aqueous solution, tested with dilute hydrochloric acid, did not form a precipitate and showed silver to be absent.

A/...

A sample of the solution was reduced with aluminium and acid and tested with mercuric chloride, with cupferron and with the cacotheline spot test, all of which showed that tin was present. A test for chloride, with silver nitrate, proved the presence of this ion in solution. A semi-quantitative test was used to establish the present of perchlorate. Two approximately equal volumes of the solution were poured into separate test tubes. The chloride in one sample was precipitated as silver chloride, while the contents of the other were first reduced with titanous sulphate and then treated with silver nitrate. As the amount of silver chloride in the reduced sample was nearly double that in the other tube, it was deduced that perchlorate was present in the original solution.

The occurrence of both silver and chlorine in the black liquid showed that at least one of these elements was present in a non-ionised form. Hill[50,51] found that silver perchlorate was not ionised in benzene, but existed mainly in the form of dimeric molecules, although monomeric and trimeric forms were present. In solution in benzene, stannic chloride is a covalent compound. It was therefore possible for both silver and chlorine to have been present in a non-ionised form. In the trial reaction, 3.83 moles of silver perchlorate were used for every mole of stannic

chloride/...

chloride. Thus it was expected that some of the excess stannic chloride would have been present in the black liquid. Furthermore the presence of silver indicated that either some silver perchlorate complex had formed or that a part of the silver perchlorate had dissolved in the black liquid and had remained unchanged.

(b) Quantitative analysis.

More samples of black liquid were prepared and used for analysis. The results of the analyses are given in table 3. It was observed that the composition of the black liquid depended on the molar ratio of the reagents that were used in the reaction. For brevity, the number of moles of silver perchlorate that were allowed to react with each mole of stannic chloride was called the "initial ratio". On the assumption that each chlorine atom in stannic chloride could react with one molecule of silver perchlorate, an initial ratio of 4 represented stochiometric quantities; values less than 4 showed that excess stannic chloride was used, while initial ratios above 4 indicated that silver perchlorate was in excess.

Table 3/...

Table 3

Analyses of black liquid

No.	Initial Ratio	% Sn	% Ag	% Cl	% ClO_4	% Total	Mol. Ratio Sn:Ag:Cl:ClO_4
1	3.91	17.1	?	15.4	38.9	?	1.00: ? :3.02:2.71
2	3.82	5.88	10.7	4.91	20.4	41.9	1.00:2.00:2.80:4.14
3	3.74	17.1	24.7	18.4	39.8	100.0	1.00:1.59:3.60:2.78
4	2.15	19.8	nil	14.5	48.1	82.5	1.00: - :2.45:2.90
5	1.37	14.2	nil	6.13	80.0	100.3	1.00: - :1.45:6.72
6	8.82	9.48	16.6	nil	47.3	73.4	1.00:1.93: - :5.96

The black liquid was analysed for silver and tin by the sulphide method (see Section F, page 121) and for chloride and perchlorate by titration with thiocyanate. Titanous sulphate was used to reduce the perchlorate. In the case of the first sample (table 3, No. 1) a different method of analysis was used. While most of the mixtures were allowed to react at room temperature, two samples, Nos. 4 and 5, were prepared at the temperature of boiling benzene.

The first sample was separated from the reaction mixture by centrifugation immediately after the stannic chloride had been added. The immiscible liquid layer was washed with anhydrous benzene and centrifuged after each wash.

Although/...

Although colourless directly after preparation, the liquid became darker in colour with each wash until it was black, as before. It appeared that the formation of the black colour could have been due to some decomposition. The black liquid was divided into six weighed samples for analysis. Two of these were hydrolysed in water and used to determine the tin content by the metastannic acid method. The remaining four parts were hydrolysed in a solution of chloride-free sodium hydroxide. After filtration, two of the alkali solutions were acidified and titrated for chloride by the Volhard method. The remaining two were used to determine total chloride and perchlorate by titanous sulphate reduction, followed by titration with thiocyanate. There was not sufficient material to determine the silver. The results of the analysis are given in table 3 (No. 1).

The next sample (No. 2) was prepared in a similar way, but was analysed by the sulphide procedure. It was observed that when the black liquid was weighed into sodium hydroxide, droplets of benzene floated to the surface. The benzene would explain the fact that only some 40% of the sample was accounted for by analysis.

The product of the third reaction was transferred to the vacuum system (figure 3) immediately after preparation. When most of the easily volatile compounds, benzene and

stannic/...

stannic chloride, had been removed the residue was analysed (table 3, No. 3). As the benzene had been distilled off, the effect observed in sample 2 was not noticed. Analysis of this sample accounted for all the material.

To test whether the black colour was due to decomposition, the samples numbered 4 and 5 were prepared under conditions more likely to decompose the product. After the stannic chloride had been added to the silver perchlorate solution in benzene, the reaction vessel was fitted with a condenser protected from atmospheric moisture, and the mixture allowed to reflux for several hours in a water-bath. When the reaction mixture had been centrifuged, a thin layer of a black powder was found covering the solid silver chloride layer. The black layer, heated in a crucible to about 500°C., was found on cooling to have deposited a mirror of metallic silver on the base of the crucible. It was therefore possible that the black colour was due to colloidally dispersed metallic silver. Both the samples were analysed, but the latter, No. 5, was treated in the vacuum apparatus in the same way as was No. 3, before analysis. These two samples were found to contain no silver, but a very small quantity of black powder remained undissolved in the sodium hydroxide, in which the samples were hydrolysed before analysis. The results of the

analyses/...

analyses of samples 4 and 5 are given in table 3.

Whereas all the previous samples had been prepared using excess stannic chloride, the next sample, No. 6, was prepared from a reaction mixture containing a large excess of silver perchlorate. The black liquid from this preparation was analysed as before and found to contain no chloride. In this respect it differed completely from all earlier preparations. It was therefore concluded that the composition of the black liquid depended on whether stannic chloride or silver perchlorate was used in excess.

An examination of the results in table 3 indicated that the black liquid did not correspond to the formation of any single compound but had to be considered as a mixture of substances. When a large excess of stannic chloride was used, samples 4 and 5, the black liquid did not contain any silver. Similarly, with excess silver perchlorate, sample 6, it contained no chloride. When, however, the reagents were used in very nearly stochiometric quantities, the black liquid contained silver as well as chloride, in addition to tin and perchlorate.

(c) Possible interpretation of the results.

The analytical results in table 3 showed that some samples contained silver, some chloride and a few contained

both/...

both silver and chloride. As the presence of silver suggested the presence of unchanged silver perchlorate and chloride, unchanged stannic chloride, it follows that both silver perchlorate and stannic chloride could dissolve in the black liquid phase. Furthermore, in the samples that contained both silver and chloride, both silver perchlorate and stannic chloride were present. It may thus be assumed that the rate of reaction in the black liquid phase was very much less than in benzene.

From the results obtained in Part 4 (see pages 75 and 81) it could be assumed that the rate of distribution of stannic chloride between the black liquid phase and the benzene phase was greater than that of silver perchlorate.

When reaction took place in the presence of a large excess of stannic chloride, the analysis of the black liquid phase showed a discrepancy between the number of equivalents of anions and cations. This discrepancy indicated that free perchloric acid formed in the reaction, presumably by a side reaction involving benzene. This point of view was strengthened by the results of the experiments discussed on pages 67 and 68.

The following assumptions were thus made in order to offer a possible explanation of the analytical results:-

(i) both/...

(i) both silver perchlorate and stannic chloride could dissolve in the black liquid,

(ii) the rate of distribution of the stannic chloride between the black liquid and the benzene phase was greater than that of silver perchlorate,

(iii) the rate of the reaction between stannic chloride and silver perchlorate in the black liquid was very much less than that in the benzene.

(iv) Some reaction involving benzene took place and formed perchloric acid.

Where the initial ratio was above 4, i.e. when excess silver perchlorate was used, the black liquid was found to contain no chloride. Any stannic chloride that might have dissolved in the black liquid would have redistributed itself after all the stannic chloride in the benzene phase had reacted with the silver perchlorate. In this way, the reaction would have proceeded until the stannic chloride had been completely used up. The silver perchlorate, on the other hand, would have dissolved slowly in the black liquid, which, at the end of the reaction, would have consisted of the product of reaction, probably a stannic perchlorate, and silver perchlorate. This was confirmed experimentally by the analysis of sample No. 6, which gave the ratio

Sn/...

$$Sn : Ag : ClO_4 = 1.00 : 1.93 : 5.96,$$

a result which indicated the presence of a mixture of stannic perchlorate, $Sn(ClO_4)_4$ and silver perchlorate in the ratio of approximately 1 : 1.95.

For values of the initial ratio slightly less than 4, i.e. when only a small excess of stannic chloride was used, it would have been impossible for all the available chloride to have reacted with silver perchlorate. During the course of the reaction some silver perchlorate and some stannic chloride could have dissolved in the black liquid. As it was assumed that the rate of solution of stannic chloride was greater than that of silver perchlorate, it was possible that at some stage the amount of stannic chloride that had dissolved in the black liquid was such that the concentration of stannic chloride remaining in the benzene phase was less than the equivalent concentration of silver perchlorate. When this stage was reached, the reaction proceeded as if the "initial ratio" had been above 4 until only silver perchlorate remained in the benzene phase. The stannic chloride, which, it was assumed, could redistribute itself faster than the silver perchlorate, would then redissolve into the benzene and continue to react with the silver perchlorate. At the same time the silver perchlorate could have dissolved in the black liquid, so that a stage

would/...

would have been reached when no silver compound was present in the benzene. The black liquid, however, would still have contained silver perchlorate as well as stannic chloride, and would on analysis have shown the presence of both silver and chloride. This was the case in the samples numbered 1, 2 and 3.

When the initial ratio was considerably less than 4, a large excess of stannic chloride was used. Under such conditions the reaction would have taken place in the benzene phase without sufficient time being allowed for any appreciable quantities of silver perchlorate to dissolve in the black liquid. Because of the large excess of stannic chloride, no effect would have been noticed if relatively large amounts of stannic chloride had dissolved in the black liquid. Samples of black liquid prepared in this way would have been expected to contain no silver. Analyses of samples 4 and 5 gave results in accordance with the above hypothesis.

In all cases where excess stannic chloride was used, analysis of the black liquid showed that the sum of the equivalent concentrations of the anions exceeded that of the cations. To explain this discrepancy the presence of free perchloric acid was assumed. While later work confirmed the presence of the acid, no indication could be

obtained/...

obtained as to the mechanism by which it was formed.

The wide divergence of the analytical results showed that the reaction was not a simple one. The assumptions made to explain this divergence were partly justified by observation during later experiments.

Attempts at purification of the black liquid.

The analysis of the black liquid, which was prepared in the presence of excess silver perchlorate, indicated that the material consisted of a mixture of silver perchlorate, stannic perchlorate and benzene. When it was prepared in the presence of excess stannic chloride, the indications were that the black liquid was different. In general the atomic ratios of tin to chloride to perchlorate were not integers. It was therefore possible that the product contained a number of perchlorates of tin produced by a stepwise substitution of the chloride atoms by perchlorate radicals. Another possibility was that organic compounds were formed by side reactions involving benzene. Various methods were accordingly used in an attempt to isolate and purify the products of the reaction between silver perchlorate and stannic chloride in benzene.

(a) Ether/...

(a) Ether extraction.

When a sample of the black liquid was shaken with anhydrous ether it became greenish, but when the ether was removed under vacuum, a few drops of apparently unchanged black liquid were recovered. Since ether extraction might have offered a means of purifying the reaction product, the procedure was applied to a fresh sample.

The black liquid was prepared by reacting each mole of stannic chloride with 2.86 moles of silver perchlorate. After centrifugation the black liquid was washed and extracted with ether in quantities of 5 to 10 c.c. until the combined ether extract measured about 150 c.c. The residue, which contained apparently unchanged black liquid, was discarded. The ethereal solution was transferred to a flask and the ether was pumped off by gradually reducing the pressure, until a dark greenish liquid remained.

Samples of this dark liquid were weighed into chloride-free sodium hydroxide. The solution was analysed for tin by the sulphide procedure, but gave no precipitate of silver sulphide. Aliquot parts of the filtrate from the stannic sulphide precipitation were boiled free from hydrogen sulphide and treated with standard silver nitrate. No precipitate formed, which showed that no chloride was present. The perchlorate content was found by titanous

reduction/...

reduction. The results of the analysis were

Sn 16.4%, ClO_4 82.2%, Ratio ClO_4 : Sn = 6.00.

Since neither chloride nor silver was found, the difference between the number of equivalents of anions and cations was assumed to be made up by hydrogen ions. On this basis, the atomic ratio was calculated to be

H : Sn : ClO_4 = 2 : 1 : 6

which indicated the presence of stannic perchlorate and 2 moles of perchloric acid. The analytical results were slightly low compared with those calculated for such a mixture:

Calculated composition of $Sn(ClO_4)_4$ and $2HClO_4$:-

Sn 16.78%, ClO_4 82.92%, H 0.30%.

The low experimental values could have been accounted for by incomplete removal of the ether. Owing to lack of material, hydrogen analyses were not attempted.

Despite the fact that the analytical results compared favourably with those calculated for a mixture of one mole of stannic perchlorate and two moles of perchloric acid, the results were not considered significant in view of the evidence obtained from the investigation of the reaction in ether (see Section D). It will be shown that stannic perchlorate slowly decomposes in ether to form perchloric acid, so that the ratio of 2 : 1 obtained above

must/...

must be considered a chance result. Although the extraction did purify the black liquid to some extent, it was not considered to be a good method of purification as it ultimately led to the decomposition of the required tin compound.

(b) Microdistillation under reduced pressure.

The apparatus shown in figure 4 was used for the distillation. A was a fine capillary which was used to introduce the liquid, and acted as an air leak during the distillation. B was the distillation bulb from which the liquid was distilled through the trap, C, into the receiver, D. The apparatus was evacuated through E. In order to prevent the condensation of atmospheric moisture in the receiver bulb, the capillary air leak was protected by a column packed as shown in figure 5.

With E connected to a pump, capillary A was dipped into a small tube containing some black liquid which was sucked into B. A water-bath was placed around B while D was cooled in a water/ice mixture. The water-bath at B was gradually heated to 85°C. and kept at that temperature until the distillation had stopped. The receiver bulb containing the distillate was sealed off at X and Y.

The first distillation was carried out on

about/...

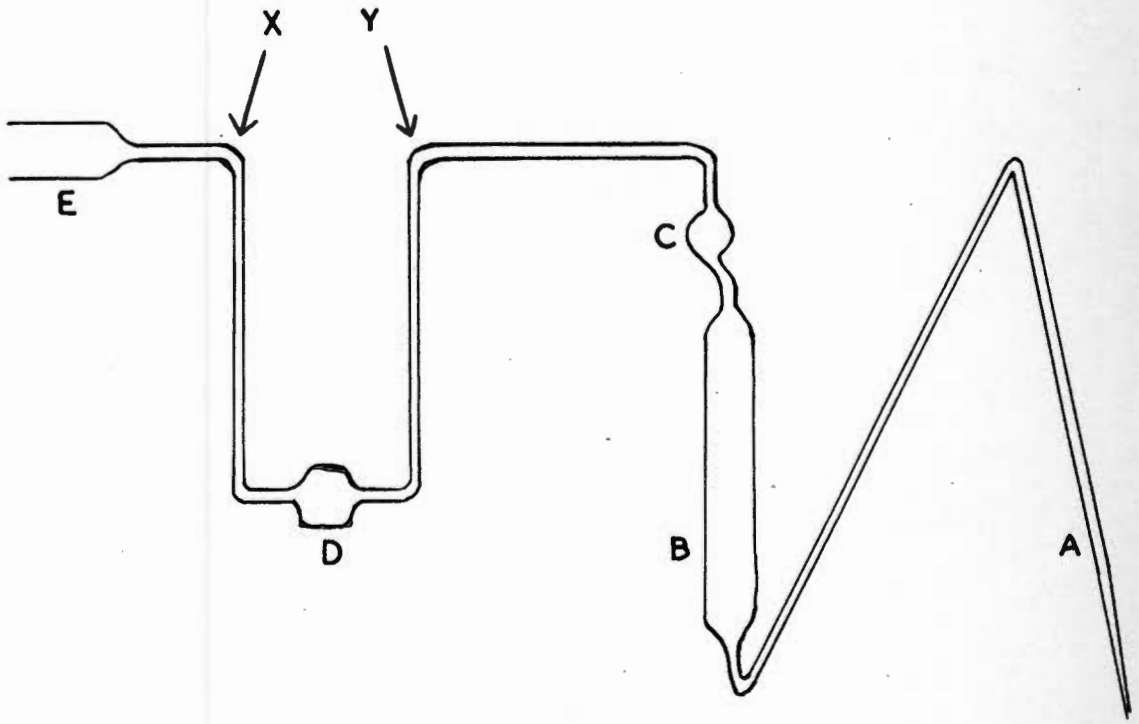


FIGURE 4

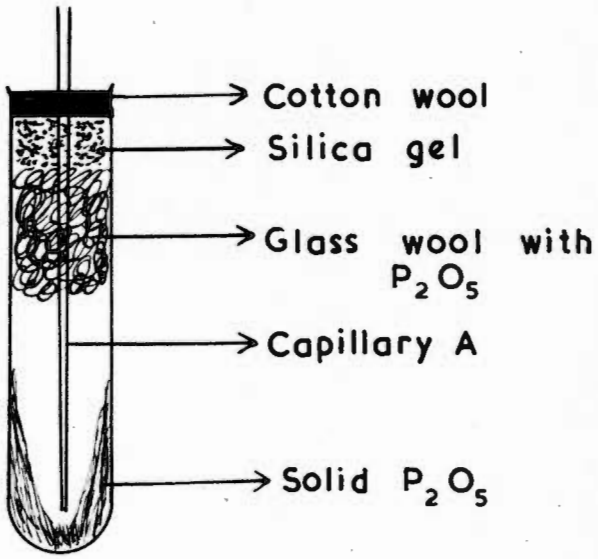

Cotton wool
Silica gel
Glass wool with P_2O_5
Capillary A
Solid P_2O_5

FIGURE 5

about 1½ to 2 c.c. black liquid and gave a mobile, colourless distillate measuring 1 to 1½ c.c. Qualitative analysis showed the liquid to contain tin. The refractive index at about 20°C. was found to be 1.374. This was very much lower than that of any known tin compound. To test whether the distillate was not simply a mixture of benzene and stannic chloride, a small drop of liquid was sucked into a capillary tube and heated behind explosion screens. The detonation which ensued could not have been produced by a mixture of stannic chloride and benzene and suggested the presence of perchlorate in the distillate. When, however, the liquid was transferred to a weighing bottle prior to being quantitatively analysed, it detonated for no apparent reason. As a result of this explosion, quantities of not more than about 0.25 c.c. of black liquid were used for later distillations and the product obtained was not more than 2 - 3 drops.

The samples of distillate were hydrolysed either in water or in standard sodium hydroxide. The calculated amounts of perchloric acid and chloride were added to bring the perchloric acid concentration to 2N and the chloride to 0.5N. These solutions were used for the polarographic determination of tin. It was interesting to note that while each sample that was hydrolysed in sodium hydroxide

gave/...

gave constant results, those hydrolysed in water showed time variation.

Figure 6 shows a polarogram (B) that was obtained from a solution of 0.00884 g. black liquid in water treated with sodium chloride and perchloric acid. When this curve was compared with that of a standard solution (A), the step on the polarogram was found to correspond to 1.8% tin. After the solution had been allowed to stand for 3 days, the tin content rose to 2.8% (figure 7). The solution was then heated for 17 hours in a thermostat at 50°C. and a polarogram again obtained (figure 8). When compared with a polarogram of a similarly treated standard solution, figure 8, the stannic content was found to have risen to 3.6%. After another 25 hours at 50°C. the value rose to 4.7%. Heat treatment could not be continued, however, as no further solution was available.

As the concentration of tin, obtained polarographically, referred only to the ionic form, it appeared that the concentration of ionised tin increased with time. Such an increase could have been due to a non-ionised tin compound which gradually hydrolysed in the presence of excess perchloric acid to form ionic tin. When the distillate was first dissolved in sodium hydroxide, however, complete hydrolysis took place before the polarographic determinations

were/...

FIGURE 6

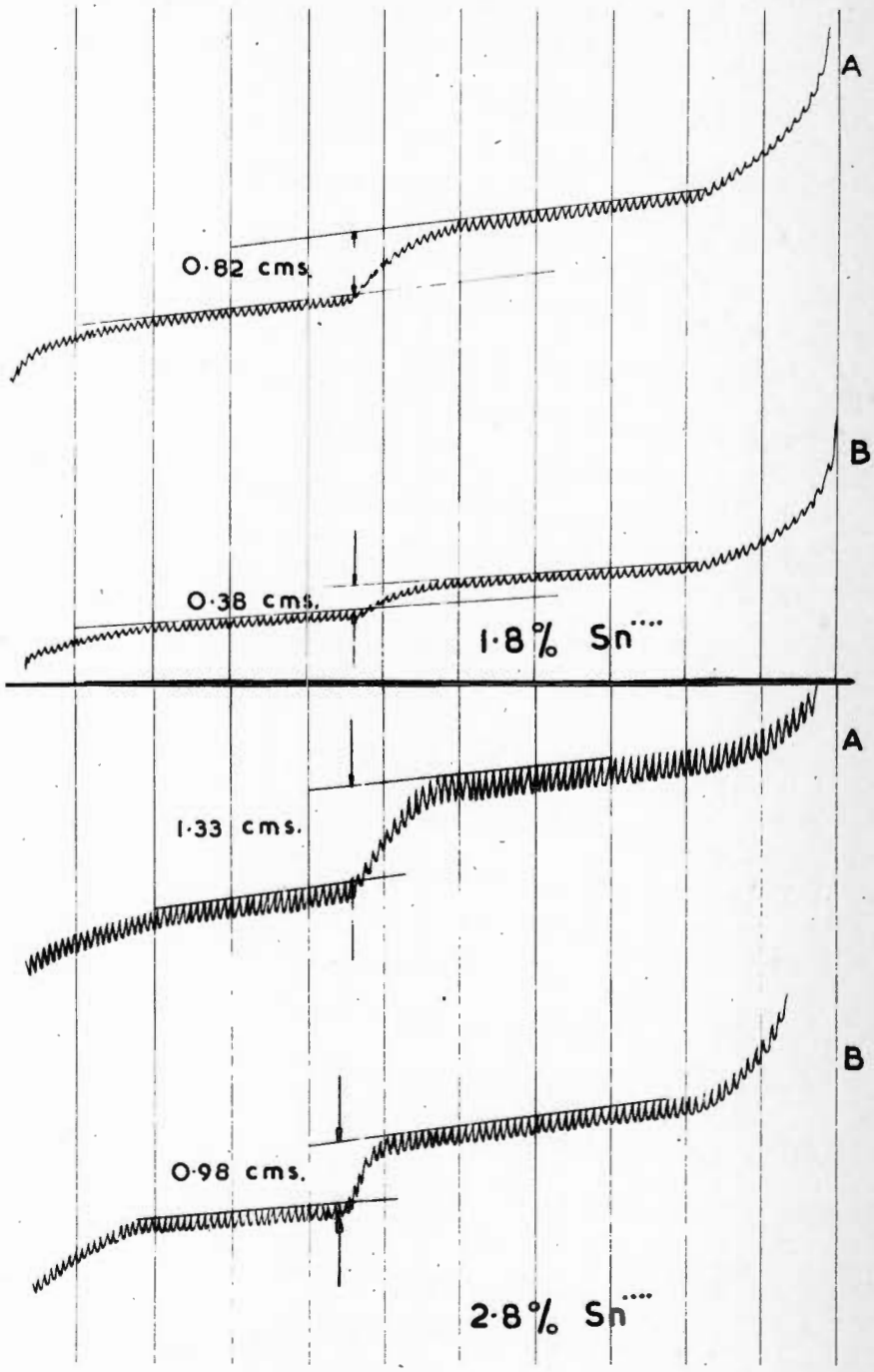


FIGURE 7

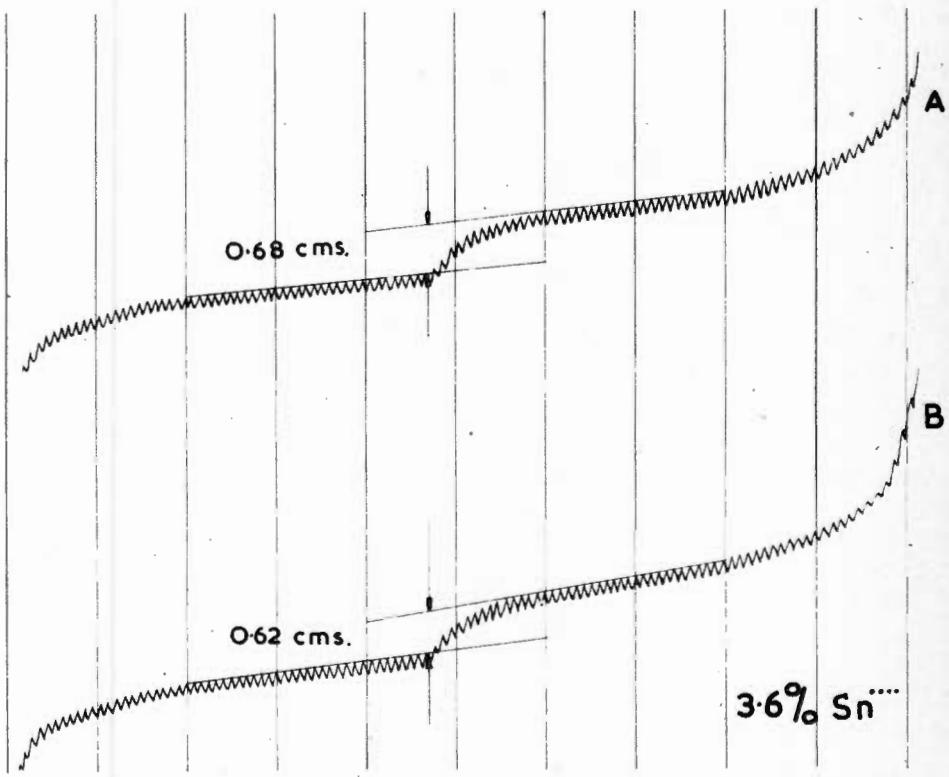


FIGURE 8

were started. In these cases all the tin was present in an ionised form and consequently polarographic analysis gave constant results.

Although the microdistillation resulted in a clear product being obtained from the original black liquid, the method was not successful in purifying the material since the various distillates contained differing amounts of tin.

(c) Microfractionation.

The apparatus used for the fractionation was a modification of that described by Shrader and Ritzer[84] and is shown in figure 9. It consisted of a boiler (A) fitted with a ground glass stopper which could be removed to introduce material. The boiler was attached to a vacuum-jacketed fractionation column (B). A condenser (C) led to the receiver. At the receiver end of the condenser a solid glass rod (D) was attached in order to guide the condensed droplets into the receiver tubes (E). These tubes were mounted on a bakelite holder fitted around a central tube (G) through which the apparatus could be evacuated. Each tube could be brought under the solid glass rod in turn to receive condensate, by turning the apparatus around the upper ground glass joint (H).

A/...

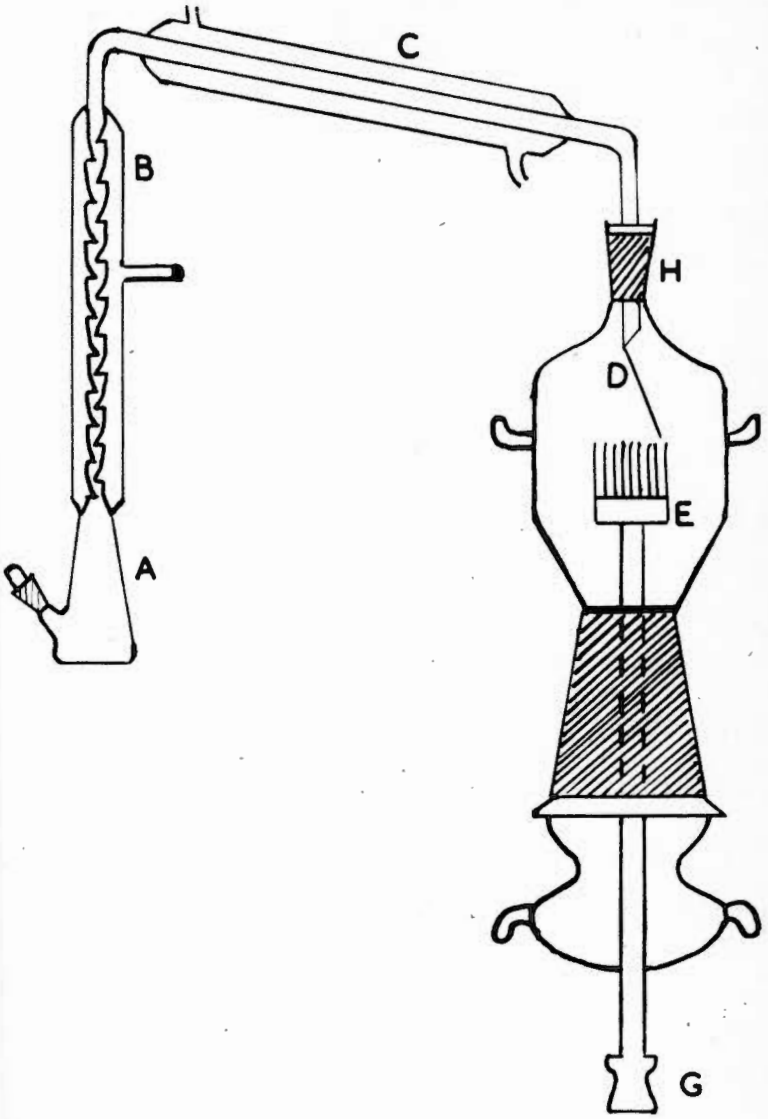


FIGURE 9

A few drops of black liquid were placed into the boiler, whose capacity was about 2 c.c. After it had been heated in a water-bath under 30 mm. pressure for about 8 hours, no distillate was obtained. Reducing the pressure to 0.1 mm. did not have any effect. The residue in the boiler was a black solid, which, even under very high magnification, showed no crystalline form.

After the stopper of the boiler had been replaced by an air leak protected from access of moisture by phosphorus pentoxide and calcium chloride, another fractionation was attempted. From this two small drops of brownish liquid distillate were obtained. The refractive indices at 25°C. were found to be 1.3745 and 1.3741 and compared favourably with the earlier value of 1.374 (see page 58). The remainder of the distillate was dissolved in sodium hydroxide. The solution was neutralised with hydrochloric acid so that, after being diluted to 50 c.c. with the calculated amount of perchloric acid, the solution contained the correct concentrations for the polarographic determination of tin. The polarograms obtained are drawn in figure 10. The curve marked A was produced by a standard tin solution which was 5.81×10^{-5} molar, while the curve B was produced by the solution of 1.753 mg. distillate in 50 c.c. The tin content was found to be 30.9% which was

too/...

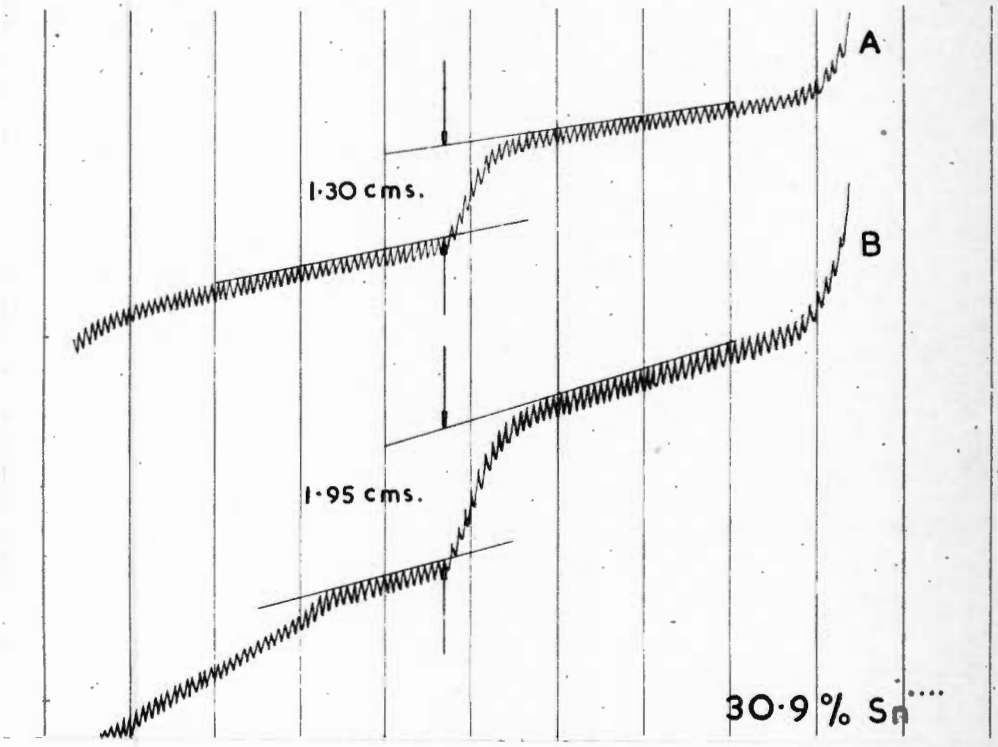


FIGURE 10

too high for pure stannic perchlorate, $Sn(ClO_4)_4$, but corresponded to an approximately equimolecular mixture of of stannic chloride and stannic perchlorate.

Another droplet, which collected on an irregularity on the glass wall of the condenser, did not run down into the receiver, but crystallised to fine white needles which easily volatilized. The rest of the volatile material distilled straight through the apparatus in the trap, which was cooled in dry ice/alcohol and was used to protect the pump from volatiles. When a third fractionation was attempted an explosion occurred. In view of the explosion, it was considered inadvisable to repeat the fractionation.

Although microfractionation did not prove a successful method for purifying the black liquid, the following two observations corroborated evidence obtained in other experiments:-

(i) the value of the refractive index was confirmed,

(ii) the crystalline compound which was observed in the condenser appeared to be similar to the volatile crystals that were obtained in the reaction between stannic chloride vapour and solid silver perchlorate (see Section E, pages 100 to 117).

(d) Vacuum/...

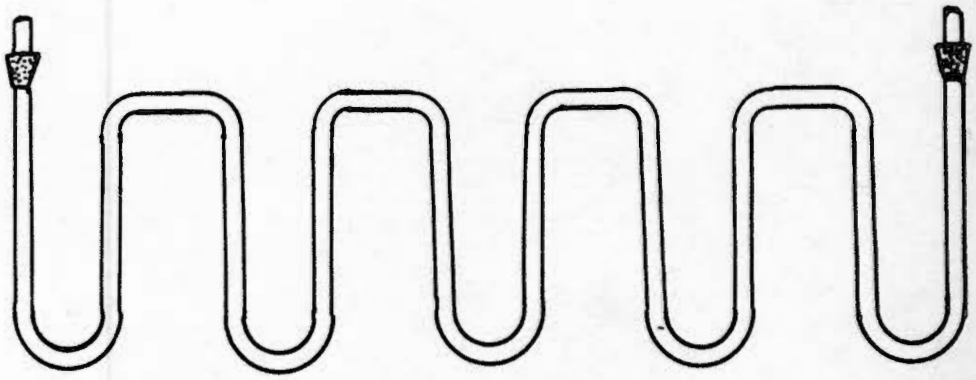
(d) Vacuum fractionation.

(i) The original black liquid.

The black liquid was transferred to a simple fractionation apparatus consisting of five U-tubes with a ground glass stopper at each end (figure 11). The tube was stoppered at one end, and, after cooling baths had been placed around each U-tube, the apparatus was evacuated through the other end. Each successive cooling bath was at a lower temperature than the preceding one. The first bath was filled with water at room temperature (17°C.) and was placed around the tube containing the black liquid. The second tube was cooled in ice at 0°C. A temperature of about -40°C. was maintained around tube number 3 by means of a mixture of tetralin and dry ice. Dry ice in alcohol kept the fourth tube at -80°C. The last tube was cooled in liquid air to prevent any volatile materials from leaving the system.

With the pump working all the time, the vacuum system was left to stand for four hours, after which it was filled with dry air and disconnected from the pump. The cooling traps were removed and the apparatus was allowed to heat up to room temperature. The solid residues in tubes 1 and 2 were soluble in hydrochloric acid and were found to contain tin, but the small amount of material made it

impossible/...



	1	2	3	4	5
Temperature :	17	0	-40	-80	-185 °C
Bath :	—	ice	tetralin	dry ice	liquid air
Product :	black solid		liquid	$SnCl_4$	C_6H_6

FIGURE 11

impossible to carry out a complete analysis. The largest fraction was found in tube 3, which contained a clear, light-brown liquid. This fraction was analysed and found to contain tin, chloride and perchlorate in the atomic ratios

$$Sn : Cl : ClO_4 = 1.00 : 2.74 : 2.17 .$$

No silver was detected. Small quantities of stannic chloride and benzene were found in tubes 4 and 5 respectively, but the separation was not complete.

The analysis of the third fraction gave results that were of the same order as those of sample 4, table 3, page 46. Apparently, therefore, vacuum fractionation of the black liquid did not result in a purified product. The importance of this experiment, however, lay in the fact that some stannic chloride and benzene, albeit in small quantities, were isolated from the original black liquid. The isolation of these materials indicated that both were present in the starting material and thus partly justified assumption (i) made to explain the analytical results (see page 51), viz. that stannic chloride could dissolve in the black liquid phase.

(ii) Product of microdistillation.

About 0.75 c.c. of a colourless liquid obtained by microdistillation of the black liquid in an apparatus of the

type/...

type shown in figure 4, were stored in a sealed tube for several months in order to test whether decomposition of the material would take place.

The sealed tube was transferred to the apparatus shown in figure 12. Since the original receiver bulb, i.e., the sealed tube containing the liquid, was sealed under a pressure of about 15 mm., the entrapped air had to be removed before the apparatus could be sealed off from the pump. In order to avoid loss of any volatile material, each U-tube of the apparatus was cooled in a liquid air trap. The steel ball, S, was lifted out of its position by means of a strong magnet and dropped from increasing heights until it broke the capillary tube of the enclosed bulb. The air inside was pumped out and the apparatus evacuated to 10^{-6} mm. Contrary to expectations, the liquid did not distil freely, but when tube C was heated in a water-bath at 80°C., distillation was completed after a further period of two hours. When all traces of the liquid had been distilled into the U-tubes, the apparatus was sealed off at D and E.

Before it was fractionated, all the volatile material was distilled into A by removing the liquid air traps around the other U-tubes. This distillation required a shorter time than the previous one and no heating was necessary. It was possible that the larger surface of the

liquid/...

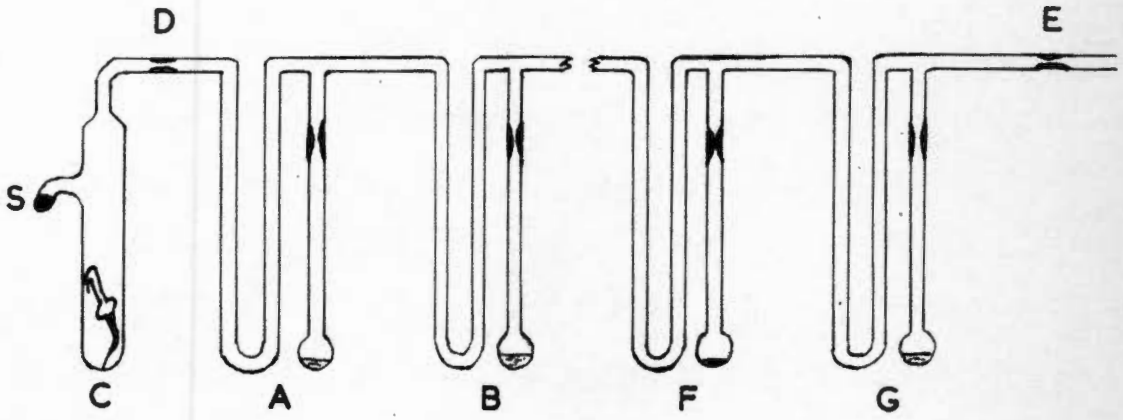


FIGURE 12

liquid, exposed in the U-tube, was the determining factor in the rate of distillation. The liquid in the vacuum system was fractionated by cooling U-tube A in a carbon tetrachloride bath at -23°C., U-tube B in an ether bath at -120°C. and tube F in a bath of liquid air. After twelve hours it was found that distillation had apparently stopped.

When the cooling baths were removed, it was found that tube B contained a mobile colourless liquid, while the residue in A consisted of a drop of light-brown liquid, the refractive index of which was 1.3741 at 25°C. The sample in A was sealed off, and on analysis, showed that tin, chloride and perchlorate were present in the molar ratios

$$Sn : Cl : ClO_4 = 1.0 : 1.7 : 16.5.$$

The liquid in B was refractionated, but as it appeared to distil as a single substance, the total distillate was removed and used for analysis. Like the fraction in A, it was found to contain no silver, but tin, chloride and perchlorate were present in the molar ratios

$$Sn : Cl : ClO_4 = 1.0 : 1.9 : 46.8.$$

The large discrepancy between the values of tin and perchlorate in both the fractions, indicated that most of the material consisted of $HClO_4$. As the total amount of tin found was very small, it seemed that during the original distillation most of the black liquid had decomposed to form

perchloric/...

perchloric acid. It was concluded, therefore, that vacuum fractionation did not lead to the purification of the black liquid.

(e) Discussion.

The methods of purification used were selected to determine whether the black liquid, prepared from excess stannic chloride, consisted of a mixture of compounds and, if so, to separate these; in particular, evidence was sought for the possible presence of stannic chloro-perchlorates. While all the attempts at purification proved unsuccessful, considerable evidence was obtained as to the composition of the black liquid.

From the values of the refractive index of aqueous solutions of perchloric acid, Mazzucchelli, Vercillo and Pro[85,86] calculated the value of the specific refraction (r), of anhydrous perchloric acid at 25°C. to be 0.2118 for the sodium D line. The work of van Wyk[87] on the density of perchloric acid in vacuo gave the result

$$D_4^{20} = 1.767 \text{ for } 100\% \ HClO_4.$$

When these values were used in the Gladstone formula

$$r = (n-1)D^{-1},$$

it was calculated that the refractive index, n, of anhydrous

perchloric/...

perchloric acid was 1.3732. While by no means conclusive, this value is near enough to the value obtained for the liquid isolated by microfractionation (see page 61), 1.374, 1.3745, 1.3741, to indicate the presence of anhydrous perchloric acid. The agreement between the calculated and the experimental values for the refractive index would have been even closer had the density at 25°C. been available, but the difference between the densities at 20° and 25°C. was considered small enough not to affect the conclusions drawn.

The value of the refractive index, the explosive nature of the distillate and the indications obtained from analytical results, taken together, pointed clearly to the presence of free perchloric acid in the black liquid.

Throughout this investigation there were no indications that stannic chloro-perchlorates were present, but the vacuum fractionation resulted in the isolation of stannic chloride and benzene. It appeared, therefore, that when the black liquid was prepared from excess stannic chloride, some stannic chloride dissolved into it in the same way as silver perchlorate did when that compound was used in excess during the preparation.

The appearance of a volatile crystalline compound during microfractionation was considered very significant,

since/...

since this was the first sign that a pure material had been isolated. Whereas all the reagents were either liquids or non-volatile solids, a volatile solid could only have been a product of the reaction. A similar volatile solid was isolated during the investigations of the heterogeneous reaction between stannic chloride vapour and solid silver perchlorate (Section E) and was proved by analysis to be stannic perchlorate. It was accordingly assumed that the crystalline material that formed in this case was also stannic perchlorate.

It was therefore concluded that the black liquid phase was a mixture, the constituents of which depended on whether excess silver perchlorate or stannic chloride was used in the reaction. In the presence of excess silver perchlorate, the black liquid contained silver perchlorate, stannic perchlorate and benzene, while with excess stannic chloride, it contained stannic chloride, stannic perchlorate, free perchloric acid and benzene.

PART 3

THE INVESTIGATION OF THE BENZENE PHASE AND THE SOLID PHASE

In addition to the black liquid phase, two other phases were present in the mixture obtained from the reaction between stannic chloride and silver perchlorate in benzene, viz. the benzene phase and the solid phase. While the more detailed investigations of the black liquid phase were proceeding, a systematic search was made for other reaction products in both these phases.

(a) The benzene phase.

The benzene phase invariably contained unreacted material which had to be removed before further investigations could be carried out. When stannic chloride was in excess, it was removed by extraction with aqueous sodium hydroxide, while excess silver perchlorate was extracted with water. The residual benzene solution was evaporated just to dryness on a water-bath. A small amount of brown residue, obtained in each case, could not be identified except to prove it to be organic. It had an odour very much like that of the chlorinated phenols but, nevertheless, gave negative results

for/...

for the tests both for chlorine and phenol. Despite numerous repetitions, the amount of material obtained was so small that even partial identification was impossible. It was therefore concluded that the benzene phase contained an unknown organic compound which was either present in very small quantities or was sufficiently volatile to escape with the benzene during the evaporation.

(b) The solid phase.

Analysis of the solid phase showed that the silver chloride content was between 98 and 100%, but when attempts were made to separate the total precipitate from the original reaction mixture, it was found impossible to remove the black liquid completely. When, however, the precipitate was centrifuged for a long time, the black liquid formed an ill-defined layer above the precipitate, so that the lower portion of the precipitate was free from black liquid and could be used for further investigation.

Successive extractions of the precipitate with various solvents in order of increasing dipole moment were made, starting with benzene or carbon tetrachloride and ending with aqueous solutions of acids and alkalis. Each extract was carefully evaporated to dryness under reduced pressure, but only the ether and the alcohol extracts were

found/...

found to contain dissolved substances. A very small amount of a crystalline solid was obtained from each of these extracts, but could not be identified. It was found that the crystalline material was organic. On heating, the material began to char at 58 - 62°C., and had completely charred at 110°C. At no stage during heating could melting be observed. An attempt to identify the crystalline compound by means of its absorption curve failed, as no absorption peaks were registered - only a slight irregularity at 272 mμ was noted. The instrument that was used was a Beckman model DU quartz spectrophotometer and measurements were taken over the whole range 200 - 1000 mμ.

It was therefore concluded that the solid phase, which consisted mainly of silver chloride, contained small quantities of unidentified organic materials. It was considered likely that these materials were formed by side reactions between benzene and either stannic chloride or stannic perchlorate.

PART 4

THE DETERMINATION OF THE REACTION RATIO

As a result of the different values obtained for the ratio of perchlorate to tin in previous experiments, it was necessary to determine the number of moles of silver perchlorate that reacted with stannic chloride. This value was termed the "reaction ratio" and was defined as the number of moles of silver perchlorate removed from the benzene phase, per mole of stannic chloride, in contradistinction to the "initial ratio", which represented the number of moles of silver perchlorate originally dissolved in benzene, per mole of stannic chloride. The first determination was carried out on a single preparation to investigate whether any change took place over a period of time. Several other determinations were made, using relatively large quantities of reagents, in order to obtain a sufficient yield of black liquid for analysis, while later experiments were carried out on smaller samples to investigate the effect of different initial ratios on the reaction ratio.

The/...

The reaction ratio in the presence of excess silver perchlorate.

(a) First determination - the effect of time on the reaction ratio.

A known weight of stannic chloride (0.4445 g.) was added to a known volume, 205.3 c.c., of benzene containing 4.2284 g. silver perchlorate. The initial ratio, calculated from the weights of the reagents used, was 11.95, which showed that there was a large excess of silver perchlorate. Precipitation took place as soon as the stannic chloride was introduced, but the reaction mixture was not allowed to stand until the precipitate had settled. Periodically aliquots of the benzene phase were removed for titration to determine the change in the silver content of the solution. The results of the experiment are given in table 4 below. The values listed in the second column correspond to the total decrease in the silver perchlorate content of the whole benzene phase.

The first sample, drawn after 5 minutes, was the only aliquot which contained any appreciable amount of silver chloride in suspension. Before titration, this silver chloride was filtered off and found to weigh 0.0050 g. While most of the precipitate was probably suspended in the benzene at the time the sample was drawn, it was possible that some

silver/...

silver chloride formed during the time taken to remove the aliquot sample. On the assumption that all the silver chloride had formed in the sampling vessel, it was calculated that the decrease in the silver content of the whole benzene phase led to a lowering of the value of the reaction ratio by about 0.18. It appeared, therefore, that the concentration of silver perchlorate in the benzene was still decreasing at an appreciable rate after about 5 minutes, but that after 30 minutes an approximately constant level had been reached.

Table 4

First determination of reaction ratio

Time after initiation hr. min.	Weight $AgClO_4$ used g.	Reaction Ratio moles $AgClO_4$: moles $SnCl_4$
5	1.714	4.85
30	1.778	5.03
32	1.772	5.01
1 - 3	1.789	5.06
1 - 5	1.778	5.03
2 - 0	1.784	5.04
2 - 5	1.784	5.04
23 - 50	1.796	5.08
23 - 56	1.796	5.08

It/...

It was observed that after nearly 23 hours the value of the reaction ratio had risen from 5.03 to 5.08. This indicated that during the period of standing, some silver perchlorate had been removed from the benzene solution. Such a decrease in the silver content of the benzene phase could have been due to a gradual distribution of silver perchlorate between the benzene and the black liquid, and would have resulted in the accumulation of unreacted silver perchlorate in the latter. Consequently, the black liquid was separated from the reaction mixture, weighed into chloride-free sodium hydroxide and used for analysis. Silver and tin were determined by the sulphide procedure and perchlorate by titanous reduction and titration with thiocyanate. No chloride was detected in the black liquid. The analytical results showed that the atomic ratio of tin, silver and perchlorate was

$$Sn : Ag : ClO_4 = 1.00 : 1.02 : 4.99,$$

and could have been explained by the formation of an equimolecular mixture of two perchlorates, that of tin, $Sn(ClO_4)_4$, and that of silver, $AgClO_4$, together with an undetermined amount of benzene. The analytical value for the ratio of perchlorate to tin (4.99) did not differ much from the value of the reaction ratio (5.08).

The results showed that although the value of the

reaction/...

reaction ratio increased slowly on standing, there was very little difference between the values obtained after 2 and after 23 hours. In later determinations the mixture was therefore allowed to stand for at least 2 hours before any aliquot portions were removed for titration.

(b) Second and third determinations - the effect of time on the silver perchlorate content of the black liquid.

As it was more convenient to weigh the benzene, the second determination was carried out with a weighed amount of benzene. The density of the solvent at the required temperature of $t^{\circ}C.$ was calculated from the equation

$$d_4^t = 0.9005-1.0636\times10^{-3}t-0.0376\times10^{-6}t^2-2.213\times10^{-9}t^3$$

where the constants were those determined by Biron[88] and by Young[89]. From the weight of the reagents used, the initial ratio was calculated to be 6.90. After the addition of stannic chloride, the mixture was allowed to stand for 6 hours and during the following 2 hours aliquots were removed every 30 minutes for titration with thiocyanate. It was found that during this period the reaction ratio remained constant at 4.86.

About a week after its preparation, the black

liquid/...

liquid was removed from the reaction mixture and analysed. Tin and silver were determined by the sulphide procedure, as before, but the perchlorate content was found by precipitation of nitron perchlorate. No chloride was detected. The analytical results gave the ratio

$$Sn : Ag : ClO_4 = 1.00 : 1.87 : 5.78$$

which could have been obtained from a mixture of stannic perchlorate and silver perchlorate in the ratio of 1 : 1.8.

The ratio of perchlorate to tin found analytically (5.78) was very much higher than the value of the reaction ratio (4.86). The increase in the number of moles of perchlorate to every mole of tin in the black liquid strengthened the earlier view that silver perchlorate dissolved in the black liquid during the time it was stored.

Conclusive proof of the solubility of silver perchlorate in the black liquid was obtained in the third determination of the reaction ratio. With an initial ratio of 13.80, the reaction ratio was found to be 5.27. The reaction mixture was then centrifuged and left to stand in the reaction tube for several weeks. After this time the black liquid was found to contain a crystalline material which proved to be silver perchlorate. The isolation of this compound clearly showed that, on standing, the black liquid gradually extracted silver perchlorate from the benzene phase.

(c) Fourth/...

(c) Fourth determination - small excess of silver perchlorate.

A fourth determination of the reaction ratio was made by dissolving 4.63 moles of silver perchlorate in benzene and allowing it to react with 1 mole of stannic chloride. After the reaction mixture had been left to stand for several hours, the supernatant liquid was analysed as before. The value of the reaction ratio was found to be 4.14. Analysis of the black liquid gave the ratio

$$Sn : Ag : ClO_4 = 1.00 : 0.18 : 4.18.$$

The analytical ratio of perchlorate to tin agreed with the reaction ratio. Since very little delay occurred between the determination of the reaction ratio and the analysis of the black liquid, the agreement between these two results confirmed that the black liquid consisted of a mixture of stannic perchlorate and silver perchlorate, even in the presence of a small excess of silver perchlorate. It should be pointed out that, as was the case in earlier analyses (see Part 2), the total material accounted for analytically was of the order of 70%. The remaining 30% was assumed to be benzene.

Reaction/...

Table 5

Determination of reaction ratio in excess stannic chloride

Time after initiation hr. min.	Weight $SnCl_4$ used g.	Reaction Ratio
45	2.109	3.01
55	2.133	2.98
1 - 35	2.124	2.99
1 - 45	2.131	2.98
2 - 30	2.120	2.99
2 - 45	2.126	2.99
3 - 0	2.127	2.98
7 - 30	2.125	2.99
23 - 0	2.119	3.00
23 - 30	2.127	2.98

The fact that the value of the reaction ratio did not change with time indicated that equilibrium between the stannic chloride in the benzene phase and that dissolved in the black liquid was attained faster than was the case with silver perchlorate. The above experiment therefore justified the assumption made in Part 2 that the rate of distribution of stannic chloride between the black liquid and the benzene phase was greater than that of silver perchlorate.

The/...

The low value pointed to the dissolution of unreacted $SnCl_4$ in the black liquid. This assumption was tested by analysis, the results of which showed that no silver was present and that the atomic ratio of tin, chloride and perchlorate was

$$Sn : Cl : ClO_4 = 1.00 : 1.94 : 3.02.$$

Although the ratio of perchlorate to tin, obtained analytically, apparently agreed with the reaction ratio, the agreement was misleading because:-

(i) the presence of chloride confirmed that some unreacted stannic chloride was dissolved in the black liquid, and

(ii) the difference between the anion and cation concentrations indicated that the black liquid contained free perchloric acid.

The presence of both these compounds was in agreement with earlier observations (see Part 2).

Multiple determinations - the effect of the initial ratio.

To complete the investigation of the reaction ratio, a series of determinations was made with varying initial ratios. Known volumes of standard solutions of stannic chloride and silver perchlorate in benzene were mixed in

different/...

different proportions, but the total volume of each reaction mixture was about 40 c.c. When the reagents had been added, the mixtures were left to stand for about 2 hours, after which two 10 c.c. aliquots of the benzene solution were removed and titrated by the Volhard method to determine the excess silver or chloride content. It was assumed that no change in volume occurred when the two standard solutions were originally mixed. No attempt was made to analyse the small amount of black liquid formed in each reaction mixture.

The results obtained for the determinations are given in table 6 and the variation of the "reaction ratio" with "initial ratio" is shown graphically in figure 13. The lower part of table 6 lists the corresponding values for the 5 determinations detailed in the preceding paragraphs.

Whereas it was theoretically expected that the reaction ratio should be constant and independent of the initial ratio, it was found that the reaction ratio varied continuously, and depended on the relative concentrations in which the reagents were mixed. This surprising observation confirmed that no single reaction could account for all the experimental evidence that had been noted in connection with the reaction between stannic chloride and silver perchlorate in benzene. The result did, however, explain the inconsistency of the composition of the black

liquid/...

liquid (see table 3) as each sample of liquid was prepared using different initial ratios.

Table 6

The effect of "initial ratio" on the "reaction ratio"

Expt. No.	Weight $SnCl_4$ g.	Weight $AgClO_4$ g.	Initial Ratio	Reaction Ratio
B1	0.0952	0.9186	12.13	5.10
B3	0.1298	0.9057	8.77	4.76
B4	0.1559	0.7607	6.13	4.43
B5	0.1729	0.5875	4.27	4.05
B6	0.2442	0.7324	3.77	3.96
B7	0.1887	0.5016	3.34	3.81
B8	0.1985	0.3871	2.45	3.47
B10	0.3514	0.4136	1.48	2.84
B12	0.3218	0.3175	1.24	2.44
1	0.4445	4.2284	11.95	5.08
2	1.1658	6.4221	6.90	4.86
3	0.6001	6.5893	13.80	5.27
4	2.0282	7.4802	4.63	4.14
5	3.5722	5.0503	1.78	3.00

It/...

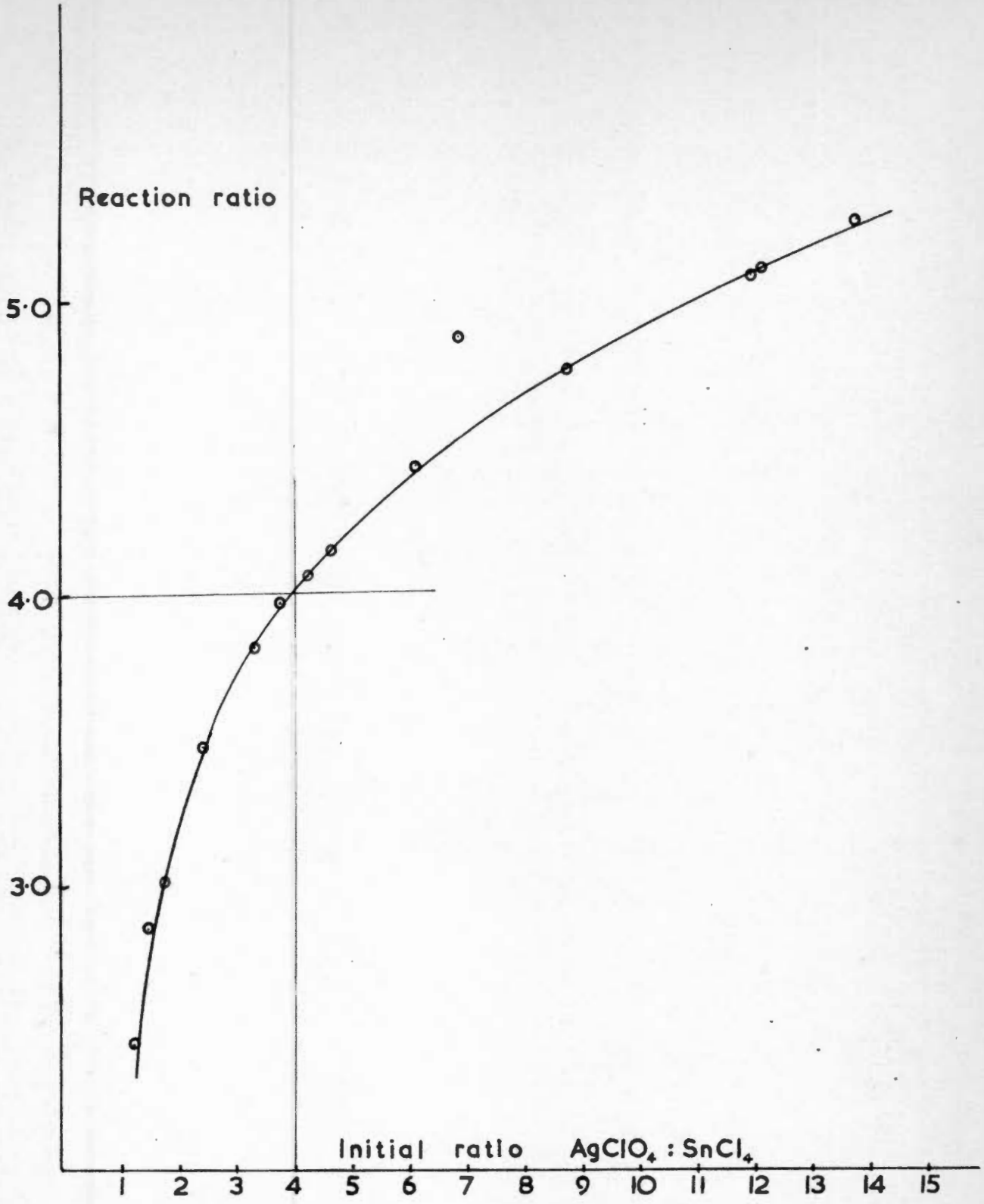

Reaction ratio
5·0
4·0
3·0
Initial ratio $AgClO_4 : SnCl_4$
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

FIGURE 13

It was of interest that the curve (figure 13), passed through the point (4,4). This showed that, when exactly equivalent proportions of silver perchlorate and stannic chloride were mixed, both were simultaneously removed from solution. Consequently, in the absence of any excess reagent it is likely that the main reaction proceeds according to the equation

$$4AgClO_4 + SnCl_4 \longrightarrow 4AgCl + Sn(ClO_4)_4.$$

Furthermore it is likely that this is the main reaction in all cases and that the complexities are due to side reactions and secondary reactions involving the solvent, the stannic perchlorate formed or the excess reagent present in the reaction mixture.

In the case of excess silver perchlorate, the shape of the curve is that expected for the absorption of this reagent by the black liquid and is in agreement with earlier analyses which indicated that the black liquid was a mixture of the stannic and silver perchlorates. A similar argument could be applied to the case of excess stannic chloride, but here the observed analytical values could not be used as a guide since they also indicated the presence of free perchloric acid. It would therefore appear that subsequent to the main reaction, a secondary reaction took place and finally led to the decomposition of the stannic

perchlorate/...

perchlorate. As decomposition took place only in the presence of excess stannic chloride, it is possible that the stannic chloride effected decomposition of the perchlorate by some unknown mechanism possibly of the Friedel-Crafts type, involving reaction with benzene, but no experimental evidence was available to test this possibility.

The results of the investigation of the reaction ratio thus served as confirmation of some observed results and as explanation for the wide discrepancies noted in the analyses.

PART 5

SUMMARY

All the experiments discussed in the preceding parts of this section showed that the products of the reaction between stannic chloride and silver perchlorate in benzene varied, and depended on whether stannic chloride or silver perchlorate was used in excess. In either case, the addition of stannic chloride to a solution of silver perchlorate in benzene produced a mixture consisting of three phases, a benzene phase which contained the excess reagent, a solid phase which consisted almost entirely of silver chloride, and a black liquid which contained the principal products of the reaction. In view of the presence of the black liquid, quantitative separation of the silver chloride was found to be impossible.

The main investigations were carried out in an attempt to ascertain the composition of the black liquid. Analysis could only indicate the atomic ratios of the constituent elements and radicals, but could not give any information as to the nature of the various compounds present together in the black liquid.

(a) The/...

(a) The reaction in excess silver perchlorate.

Whenever the reaction was carried out in the presence of excess silver perchlorate, the black liquid was shown by analysis to consist of a mixture of benzene, silver perchlorate and stannic perchlorate. This view was strengthened by the determination of the reaction ratio, i.e., the determination of the number of moles of silver perchlorate removed from the benzene phase per mole of stannic chloride. The values of the reaction ratio depended on the initial ratio, i.e., on the number of moles of silver perchlorate originally added per mole of stannic chloride. Although the reaction ratio increased with initial ratio, the increase was due to the absorption of unreacted silver perchlorate by the black liquid. It appeared that, in the presence of excess silver perchlorate, the reaction was a straightforward one, according to the reaction

$$SnCl_4 + 4AgClO_4 \longrightarrow Sn(ClO_4)_4 + 4AgCl.$$

(b) The reaction in excess stannic chloride.

Unlike the case of excess silver perchlorate, the reaction in excess stannic chloride presented serious complications. The most important of these was that the analysis of the black liquid showed it to contain more

anions/...

anions, chloride and perchlorate, than could be accounted for by the equivalent concentration of tin. The difference between the anion and cation concentrations was assumed to have been made up by hydrogen ions present in the form of free perchloric acid. While this free perchloric acid was not isolated and identified, numerous indications as to its presence justified the above assumption.

As the formation of perchloric acid would, of necessity, have involved reaction with benzene, the only compound containing hydrogen, it was expected that some organic compound would form, but no such compound was found. It should be noted, however, that during the investigation of the benzene phase and the solid phase (Part 3) unidentified organic compounds were isolated.

The determination of the reaction ratio showed that as the relative amount of stannic chloride in the reaction mixture increased, so also did the amount of stannic chloride removed from the benzene phase. This observation confirmed that stannic chloride dissolved in the black liquid, a result which was corroborated by analytical evidence and by the actual isolation of unreacted stannic chloride from a sample of the black liquid.

A strong indication that stannic perchlorate had been prepared, was obtained when a small sample of distillate

crystallised/...

crystallised to fine white needles. This crystalline compound was volatile and could only have been a reaction product. In Section E the isolation of a similar crystalline compound, consisting of fine white needles, was effected by distillation techniques and was proved by analysis to be stannic perchlorate.

It should be emphasised that all these experiments were carried out under strictly anhydrous conditions. Most of the experimental difficulties arose from the necessity of excluding all moisture, as even traces of water interfered with the reaction. In the light of this knowledge it is clear that Østerud and Prytz[39] could not have prepared stannic perchlorate by their use of aqueous perchloric acid.

SECTION D

REACTION IN ETHER

REACTION IN ETHER

Description of the apparatus.

The apparatus that was used is shown in figure 14. Dry ether was poured onto a thick layer of solid phosphorus pentoxide in each of two 500 c.c. round-bottomed flasks, A and B. Anhydrous stannic chloride was prepared by the method outlined in Section A and was contained in a sealed tube which narrowed down to a fine capillary. This tube was placed, capillary downwards, into an L-shaped tube, C. A steel ball, for breaking the capillary when the stannic chloride was required, was placed in C which was connected to a U-tube, D, into which the stannic chloride could be distilled. The combined system of A, C and D was connected through a condenser to a separating funnel, E, protected from atmospheric moisture by a bulb of phosphorus pentoxide. B was similarly connected to a separating funnel, F.

The two separating funnels fitted into the limbs of a Y-shaped tube, the lower end of which passed through a large rubber stopper. A filter stick, H, joined to two small U-tubes, L, also passed through the rubber stopper. L was connected to a large round-bottomed trap, M, which in turn, was joined to a two-necked flask, N. A vacuum fractionating system, P, was joined to N and sealed onto the

vacuum/...

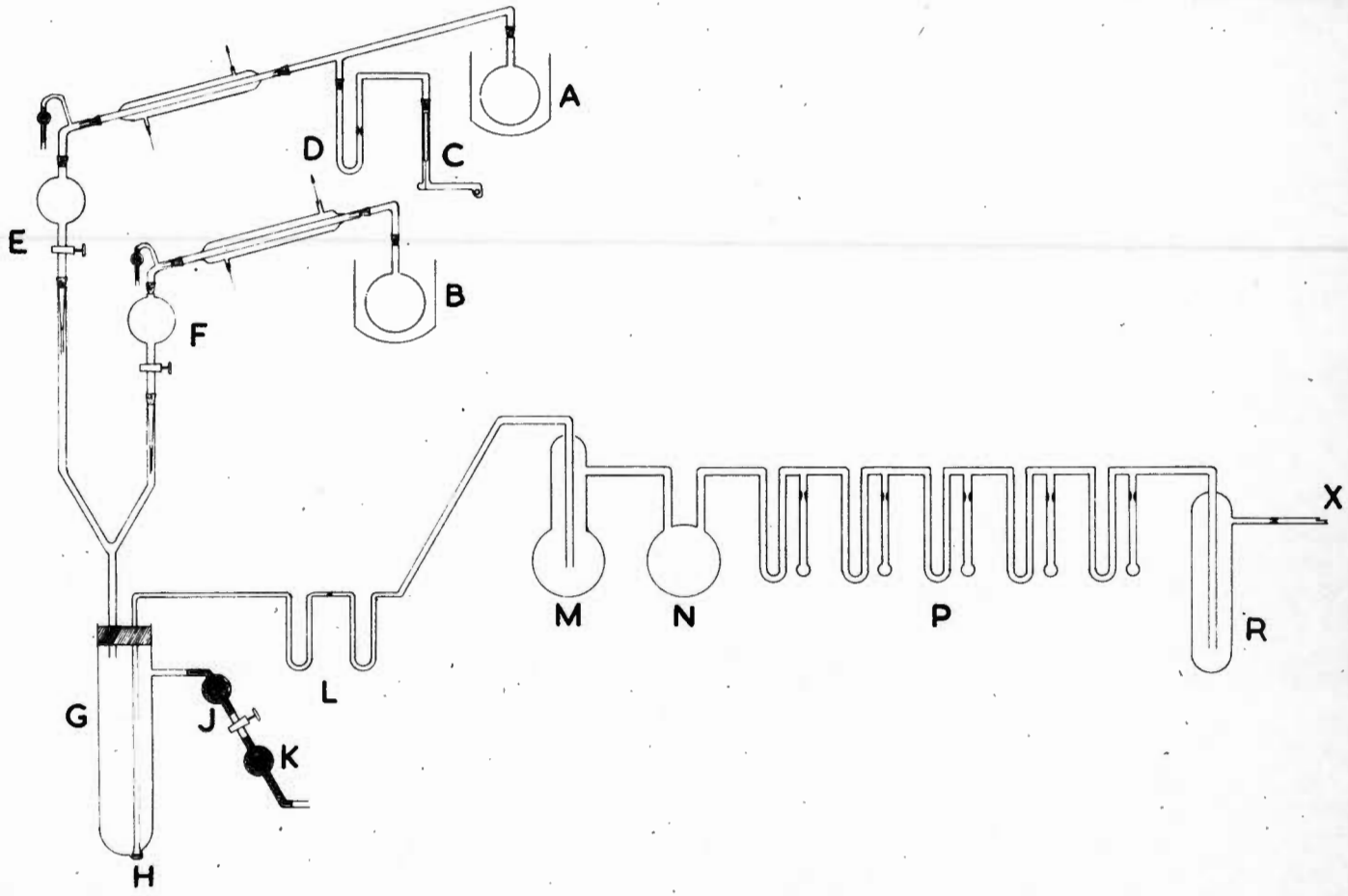


FIGURE 14

vacuum apparatus shown in figure 2 by means of the tube X. A trap, R, separated P from the other vacuum system. The reaction vessel, G, which was protected by bulbs containing phosphorus pentoxide, J, and calcium chloride, K, separated by a vacuum tap, could be fitted onto the rubber stopper in such a way that the filter stick, H, just fitted into the cavity at the bottom of the tube.

The reaction in ether.

Anhydrous silver perchlorate was placed in G and after the outlets to the air were sealed, the whole apparatus (figure 14) was evacuated. The vessel G, containing the silver perchlorate, was then immersed in a glycerol bath at 120°C. and kept at that temperature for several hours to drive off any moisture that had been absorbed by the salt. During this time, the ether in A and B was kept frozen in liquid air to prevent loss by distillation. When all traces of moisture had been removed from the system, dry air was introduced into the apparatus. The sealed phosphorus pentoxide tubes above E and F were opened and the cooling trap around the ether bulb, B, was removed.

The capillary sealed tube in C was now broken by the steel ball externally controlled by a magnet, and the stannic chloride was distilled into D. When all the stannic

chloride/...

chloride had been removed, the tube C was sealed off at the constriction. A glycerol bath was placed around D and heated to about 120°C. to distil stannic chloride, which condensed on the condenser walls and slowly drained into E. The ether distilled into E by placing a water-bath at 45 - 50°C. around A. The condensed ether at first formed a solid complex with the stannic chloride droplets in the condenser, but further distillation of ether dissolved the complex. The ethereal solution of stannic chloride was kept in E. Simultaneously the ether from B was distilled into F.

Before the ether was run into G it was necessary to open the tap between J and K, so that the displaced air could escape. At the same time a pressure had to be applied through X to prevent any ether from entering the filter stick, H. After the ether had been run onto the silver perchlorate the apparatus was gently tapped to produce a movement of the ether. This facilitated the dissolution of silver perchlorate.

The tap of E was slowly opened and the stannic chloride solution was allowed to drip into G. As each drop fell into the solution a fine white precipitate formed, and was allowed to settle before the addition of further drops of the tin solution. In this way, it was possible

to/...

to stop the addition of stannic chloride when no further precipitation took place, and to ensure that only a small excess of stannic chloride was used. When this stage was reached, the pressure that had been applied at X was replaced by gentle suction which allowed the solution to be filtered slowly through H and to be collected in M. It was essential to filter the solution very slowly, since the silver chloride formed did not coagulate, but remained as a fine suspension in the ether. Even with slow filtration, however, a small amount of silver chloride was carried over into M. After the reaction mixture had been filtered, ether from F was used to wash the residue in G. Several washes with relatively large volumes of ether were carried out, not only to wash the silver chloride in G free from ether-soluble material, but also to ensure that no products remained in the long glass tube between H and M.

After the wash liquid had been transferred to M, the receiver bulb was cooled in liquid air and liquid air traps were placed around the U-tubes at L to prevent ether vapour from coming in contact with the heated glass when the apparatus was sealed at the constriction.

Since the solution in M had carried over a small amount of silver chloride, it was necessary to distil the mixture from M to N. A liquid air bath was placed

around/...

around N and the distillation proceeded smoothly for some time, but the ether, which had solidified on the upper walls of N, ultimately caused a blockage in the neck of the flask and stopped the distillation. When this was observed, the liquid air bath was slightly lowered, but the pressure which had built up in M was sufficient to push some of the liquid from M right through the whole train into R and along X. This unfortunately resulted in small amounts of silver chloride being deposited in each U-tube and bulb of P. It therefore became impossible to recover the silver chloride quantitatively, and to obtain absolutely pure samples from later fractionations.

From the studies of the reaction products formed in benzene, it was known that the reaction product was not sufficiently volatile to distil rapidly at -23°C. Consequently, carbon tetrachloride cooling baths at this temperature were kept around three of the U-tubes of P while the ether was pumped out of the system. When most of the ether had been removed, a small amount of liquid remained in N and in the first of the cooled U-tubes. Liquid air baths were placed around the last two U-tubes of P and after the vacuum system had been evacuated to 10^{-6} mm., the apparatus was sealed off at the constriction in the tube X. The product, condensed in the cooled bends, was fractionated.

The/...

The fractionation of the liquid product was carried out by cooling the liquid to -23°C. and allowing it to distil through traps at -45°C., -60°C. and -80°C. to a tube cooled in liquid air. Distillation was very slow, but after some time when it appeared that distillation had reached a low constant rate, the residual fraction was transferred to a bulb which was then sealed off. The same process was repeated until four fractions had been collected. The last fraction was obtained by cooling the bulb in liquid air for a long time to condense all the volatile material.

The size of the fractions was purposely kept as small as possible since the experiments in benzene (Section C) had shown that the distilled reaction product was highly explosive.

Each sample was analysed for tin, silver, chloride and perchlorate. Since each fraction contained some solid material which had been blown through the apparatus, and since the solid material was assumed to be silver chloride, a small amount (equivalent to the silver content of each sample) was subtracted from the total chloride content. Although the use of such a correction presupposed that no silver was present in the form of volatile material, the assumption was justified by the fact that the reaction in benzene showed no distilled product to

contain/...

contain silver. The results of the analyses of the fractions are given in table 7. The chloride content given is the value corrected for the presence of silver chloride.

Table 7

Analyses of fractions from reaction in ether

No.	Weight fraction g.	% Sn	% Cl	% ClO_4	% AgCl	% Total	Ratio Sn:Cl:ClO_4
1	0.1740	21.0	0.25	77.9	0.62	99.8	1.00:0.04: 4.43
2	0.0914	12.7	0.27	85.9	0.51	99.4	1.00:0.07: 8.07
3	0.1831	7.40	nil	91.2	0.63	99.2	1.00: - :14.7
4	0.2327	4.53	nil	94.6	0.17	99.3	1.00: - :24.9
5	0.1671	2.22	nil	60.2	0.43	62.9	1.00: - :32.4

The analyses of the fractions show an interesting trend in the ratio of tin to perchlorate. In all the fractions, there was an excess of anions, but the excess was least in the first fraction. Only the first two fractions contained chloride, which may have been due to the presence of a small amount of excess stannic chloride. The large excess of perchlorate clearly showed that perchloric acid had formed. On this basis it was deduced that stannic perchlorate decomposed to form perchloric acid. The hydrogen was presumably supplied by a small quantity of

ether/...

ether which constituted some 37% of the last fraction. Since each fractionation required about 50 hours, it was feasible that decomposition would have become more pronounced as fractionation proceeded. As the ratio of perchlorate to tin in the first fraction was nearest to 4 : 1, it was surmised that the main product of the initial reaction was probably stannic perchlorate.

After fractionation, the silver chloride in the apparatus was removed and found to weigh 0.9154 g. From the original weight of silver perchlorate, 1.6012 g., and the analytical values given in table 7, it was possible to calculate that the recovery of perchlorate, based on the initial weight of silver perchlorate was 91.3%, while that based on the recovery of silver chloride was 83.0%. Since a small amount of material was lost as a result of the blockage during distillation, such a high percentage of recovery indicated that the silver perchlorate reacted quantitatively. This assumption was further strengthened by the fact that no unreacted silver perchlorate was detected. It was therefore concluded that the main reaction that took place was

$$4AgClO_4 + SnCl_4 \longrightarrow 4AgCl + Sn(ClO_4)_4.$$

The/...

The ether appeared to play a part in the over-all reaction, even though, as was the case in benzene, the reaction with the solvent was probably secondary to the main reaction. In view of the complications introduced by the presence of a solvent it was considered advisable to abandon this part of the investigation.

SECTION E

HETEROGENEOUS REACTION BETWEEN STANNIC CHLORIDE VAPOUR and SOLID SILVER PERCHLORATE

HETEROGENEOUS REACTION BETWEEN STANNIC CHLORIDE VAPOUR AND SOLID SILVER PERCHLORATE

Although a study of the reaction in benzene and in ether indicated the formation of stannic perchlorate, the pure material could not be isolated owing to interference by the solvent. In an effort to obtain a pure material, anhydrous stannic chloride vapour was repeatedly distilled through a plug of solid silver perchlorate. Reaction took place at the surface of the solid and the product was successfully separated from unreacted stannic chloride by repeated fractionation with a relatively small temperature difference between the distillation and receiver bulbs. While the fractionation did not result in a quantitative separation, a small amount of pure stannic perchlorate was isolated.

Preliminary reaction.

A small vacuum system, consisting of several U-tubes joined together, was used for the preliminary experiment. At the one end was a B 14 Quickfit socket into which a bulb containing stannic chloride could be fitted. The other end of the apparatus was attached to the pump. The second U-tube was packed with solid silver perchlorate

and/...

and the two ends of the plug were covered with glass wool to prevent any solid from being wafted into another part of the apparatus during the initial evacuation. After this tube had been sealed into position, a drying-tube of phosphorus pentoxide fitted with a tap, was connected at the joint at the end of the train, and the apparatus evacuated. The silver perchlorate was dehydrated and last traces of moisture were removed by flaming the apparatus at 10^{-6} mm. pressure.

After dry air had been allowed to enter the apparatus through a column of phosphorus pentoxide, the phosphorus pentoxide column was replaced by a weighed bulb containing purified stannic chloride and the system once more evacuated. Some stannic chloride was distilled into the apparatus through the tap and ground glass joint and condensed in the first U-tube. When sufficient stannic chloride had been introduced, the tube was sealed off to remove lubricated parts from the system. The bulb was weighed to determine the weight of stannic chloride that had been introduced into the apparatus. It was noticed that, even in the short time required for the distillation of stannic chloride, the grease at the tap was darkened. Since the interaction of tap grease and stannic chloride could produce hydrogen chloride, it was decided to eliminate the use of a tap from later experiments.

The/...

The stannic chloride was distilled through the silver perchlorate plug 19 times. While at first no change was observed, it was noticed, in the later distillations, when only a small drop of liquid remained, that crystallisation occurred before the last trace of liquid volatilized. After distillation backwards and forwards for 12 days, the volatile material was distilled into a U-tube at the end of the train and the tube containing the silver perchlorate was sealed off. The volatile matter was then fractionated and four approximately equal volumes of liquid were collected. Analysis showed that, although each fraction consisted mainly of stannic chloride, a small amount of perchlorate could be detected. In the presence of relatively large quantities of stannic chloride, the experimental error in determining small amounts of perchlorate was very great. It was significant, however, that perchlorate was detected in the volatile fractions. Another significant fact was that, although the silver perchlorate plug contained no tin, it was found to contain 0.1051 g. of silver chloride. The analytical figures for the volatile fractions showed no discrepancy between the anion and cation contents, which indicated that the product consisted only of stannic chloride and a perchlorate of tin. These indications prompted further investigations in this direction.

Quantitative/...

Quantitative investigation of the heterogeneous reaction

A vacuum train, similar to the one used above, was set up to investigate the interaction between stannic chloride vapour and solid silver perchlorate. This apparatus differed from the previous one by the inclusion of small bulbs next to each U-tube of the train in order that the fractions might be sealed off in the bulbs instead of in the U-tubes. Another difference was that no tap was used for introducing the stannic chloride. Instead, the stannic chloride was distilled into a small bulb with a long, thin-walled neck. A short length of pressure tubing fitted over the neck of the sealed bulb and connected it to the vacuum system. When the stannic chloride had to be introduced, the rubber tubing was bent to break the neck of the bulb. After stannic chloride had been distilled into the apparatus, the tube through which the distillation took place was sealed off and the glass fragments of the bulb weighed to determine the weight of stannic chloride that was used for the reaction. The plug of silver perchlorate had been prepared in the same way as before and the apparatus and silver perchlorate were dehydrated before the stannic chloride was introduced.

When the stannic chloride had been distilled through the silver perchlorate more than 30 times, all the

volatile/...

volatile material was distilled into a U-tube and the silver perchlorate tube was sealed off. Its contents were dissolved in aqueous ammonia. No insoluble material was detected at this stage, so that it was unlikely that any tin was present. The ammoniacal solution was carefully acidified with chloride-free nitric acid to precipitate silver chloride. This precipitate was filtered, washed free from silver perchlorate and weighed.

The volatile materials remaining in the apparatus were fractionated by repeated distillations from -23°C. to -35°C. into four fractions which were used for analysis. The tin, chloride and perchlorate contents of the fractions are given in table 8 and are expressed in millimoles. The corrected ratio of perchlorate to tin is the value that was obtained when allowance had been made for a quantity of tin, equivalent to the chloride content, being present as stannic chloride. The percentage recovery of tin and chloride was calculated from the weight of stannic chloride introduced into the system, while the recovery of perchlorate was calculated from the silver perchlorate equivalent to the recovered weight of silver chloride. The results clearly show that stannic perchlorate, $Sn(ClO_4)_4$, formed in the reaction and that two pure fractions were isolated.

Table 8/...

Table 8

Analysis of fractions from first vapour reaction

Fraction No.	Sn milli-moles	Cl milli-moles	ClO_4 milli-moles	Ratio Sn:Cl:ClO_4	Corrected Ratio ClO_4/Sn
1	0.2725	nil	1.0880	1: - :4.00	4.00
2	2.1630	8.310	0.3383	1:3.84:0.15	3.96
3	0.1506	0.1960	0.4125	1:1.30:2.74	4.06
4	0.0940	nil	0.3711	1: - :3.95	3.95
$AgClO_4$ plug	-	2.1740	-		
Total recovered	2.6801	10.680	2.2099		
Total used	2.881	11.524	2.174		
% Recovery	93.0	92.7	101.7		

The introduction of stannic chloride in the above experiment was not entirely satisfactory, since it was impossible to ensure that the inner walls of the pressure tubing were completely dehydrated. Consequently, the experiment was repeated in a similar apparatus, into which the stannic chloride was introduced from a sealed capillary. The capillary was inserted in an L-shaped tube and broken by means of a steel ball (see C, figure 14). In all experimental details, the procedure used was the same as that described for the former experiment. The results obtained are given

in/...

in table 9. The values for the tin, chloride and perchlorate contents are again expressed in millimoles. The corrected ratio and the percentage recovery are calculated as before. At an early stage in the experiment it was observed that crystalline material in the form of long thin needles had formed. These crystals were separated as fractions 3 and 7 and were analysed by micro methods.

Table 9

Analysis of fractions from second vapour reaction

Fraction No.	Sn milli-moles	Cl milli-moles	ClO_4 milli-moles	Ratio Sn:Cl:ClO_4	Corrected Ratio ClO_4/Sn
1	2.584	10.250	nil	1:3.96: -	-
2	4.807	18.820	nil	1:3.91: -	-
3	0.00078	nil	0.00308	1: - :3.95	3.95
4	2.077	7.728	0.5766	1:3.72:0.28	3.98
5	0.4254	1.541	0.1612	1:3.62:0.38	4.02
6	0.2754	0.5138	0.5866	1:1.87:2.13	3.99
7	0.00431	nil	0.0177	1: - :4.10	4.10
$AgClO_4$ plug	-	1.339	-		
Total recovered	10.17	40.19	1.345		
Total used	10.39	41.56	1.339		
% recovery	97.9	96.7	100.4		

The/...

The analysis of the crystalline material.

Since fractions 3 and 7 (see table 9) were crystalline samples, it may be of interest to record some of the analytical values in greater detail. The tin was determined polarographically and the perchlorate by microdiffusion (see pages 126 and 134). For each of these two fractions five separate polarographic determinations of tin were carried out. The perchlorate values given are chosen at random from a larger number of analyses. In all, ten determinations of perchlorate were carried out on sample 3 and fourteen on sample 7. The results agreed with each other, with an accuracy of better than 2%. Although four determinations of chloride were attempted for each fraction, no chloride could be detected by the microdiffusion method. The results are given in table 10. The unknown solution measured 20 c.c., 2 c.c. of which were made up to 5 c.c. for the polarographic determination. The tin and perchlorate values reported are calculated for the total original solution (see table 10).

From these analytical results it was concluded that the volatile crystals that had been isolated were samples of pure stannic perchlorate.

Table 10/...

Table 10

Analyses of the crystalline fractions

Polarogram step (cm.)	Polarogram step standard solution [3.92×10^{-5}M Sn] (cm.)	Sn millimoles	ClO_4 millimoles	Ratio ClO_4/Sn
Fraction 3				
0.72	1.82	0.00077_5	0.00307	3.96
0.72	1.83	0.00077_1	0.00305	3.95
0.77	1.96	0.00077_0	0.00310	4.02
0.74	1.85	0.00078_4	0.00308	3.93
0.75	1.87	0.00078_6	0.00311	3.96
Fraction 7				
2.07	0.95	0.00428	0.0178	4.16
2.18	0.98	0.00436	0.0177	4.06
2.11	0.96	0.00431	0.0173	4.01
2.17	1.00	0.00425	0.0176	4.14
2.12	0.95	0.00438	0.0180	4.11

Attempts at increasing yield of stannic perchlorate.

It was considered that the low yield of stannic perchlorate and the relatively large amounts of unreacted stannic chloride and silver perchlorate that remained, were due to the formation of silver chloride on the available

surface/...

surface of silver perchlorate. Once this surface was covered, the reaction could no longer proceed.

As a result, it was considered likely that a better yield of stannic perchlorate could be obtained if the silver perchlorate were deposited on a material with a large surface, instead of being used in the form of a plug. An experiment was carried out to test this assumption.

(a) Description of apparatus.

The apparatus that was used (figure 15) consisted essentially of five units separated from each other by capillary seals which could be broken when required by means of suitably placed steel balls. The first of these units was a simple flask, A, which contained sodium-dried ether together with a thick layer of phosphorus pentoxide. Before the flask was stoppered, the ether was slightly warmed to displace as much of the air as possible. The second unit, joined to A by means of a capillary seal, B, consisted of a two-necked flask, C, and a bulb, E, into which anhydrous silver perchlorate had been placed. A sintered glass filter plate, F, was attached to the neck of E and sealed with a capillary seal, G. This unit could be evacuated through the side-arm, D.

The silver perchlorate was heated to 120°C. and

kept/...

kept at that temperature for over 6 hours under a pressure of 5×10^{-6} mm., and, after it had been dehydrated, the outlet, D, was sealed off at the constriction.

The third unit consisted essentially of a wide glass tube, H, packed with powdered asbestos. This asbestos had been purified by repeated extractions with boiling hydrochloric acid, after which it had been ignited to 600°C. The glass tube had an inlet, J, at one end and was sealed onto a capillary seal, G, at the other. A tap was set in J to enable the column to be disconnected from the pumping system (not shown in the diagram). While this unit was being evacuated, the column H was heated to 250°C. by an external resistance furnace in order to dehydrate the asbestos.

At a later stage the remaining units of the system were attached at Q and at N. The unit attached at Q consisted of two U-tubes and bulbs, R, and a large tube, S, into which a sealed capillary containing purified stannic chloride, had been placed. This system was evacuated to 10^{-6} mm., and sealed off at the constriction in T. A similar system, P, was attached at N and included a U-tube, M, packed with solid anhydrous silver perchlorate to ensure that an excess of this salt was present in the subsequent reaction.

(b) Experimental/...

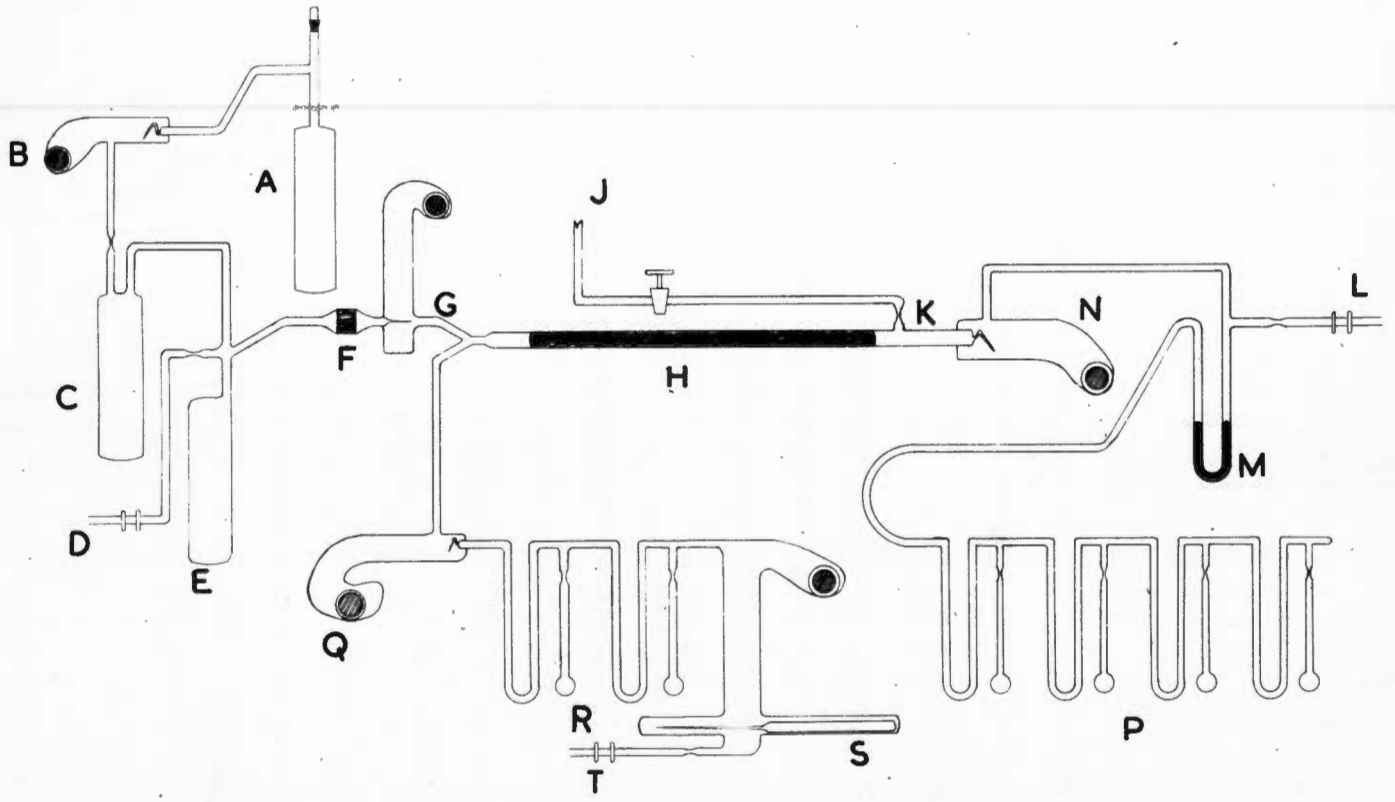


FIGURE 15

(b) Experimental procedure.

While the asbestos was being dehydrated, capillary B was broken by the steel ball to allow the ether to distil from A to C. When all the ether had been redistilled from C onto the silver perchlorate in E, the neck of tube C was sealed at the constriction. By gently tapping the apparatus, some silver perchlorate was dissolved in the ether. The whole apparatus, consisting of the second and the third units, was turned through 90° to allow the solution, which carried with it some undissolved silver perchlorate, to flow onto the filter plate, F. Capillary G, broken by the steel ball, had a very small cross-section so that the ethereal solution of silver perchlorate filtered slowly through F. The clear solution was allowed to run down the asbestos column, H. When the whole column had been wetted with the ethereal solution, the apparatus was tilted back to its original position. Bulb E was then cooled in liquid air to condense the ether that had been absorbed by the asbestos, with the result that the dissolved silver perchlorate was left deposited on the asbestos column. The process was repeated until most of the silver perchlorate had been transferred from E to H.

The tap in J was opened and the ether was slowly pumped off from E through J into traps (now shown in the

diagram/...

diagram) cooled in liquid air. During this pumping process, the air that had originally been trapped in A, was also removed. The system was pumped down to 5×10^{-6} mm. and kept at the pressure for 3 hours before it was sealed at the constriction, K.

The fourth and fifth units were now attached at Q and at N and after each part of the apparatus had been evacuated, the capillaries at Q and N were broken and the whole system evacuated to 10^{-6} mm. through L. Pumping was continued for 37 hours to ensure the removal of all volatile materials. The system was finally sealed at the constriction in L.

All the parts of the apparatus onto which silver salt had been desposited, were painted black to prevent decomposition by light. As soon as the stannic chloride capillary was broken, the reaction was started by distilling the stannic chloride through the asbestos column and the silver perchlorate plug into the train, P. Distillation was very slow; even after 4 days not all the stannic chloride had been condensed. After that period of time, the liquid was redistilled into T.

Owing to a temporary shortage of liquid air, the bulb with condensate was allowed to stand at room temperature overnight, but by the following morning, no liquid could be

seen/...

seen in any part of the system. Since the weight of stannic chloride that was used was more than sufficient to allow it to build up its own vapour pressure throughout the whole apparatus, it was expected that liquid would remain. As no liquid was found, it was considered that the asbestos column had absorbed the stannic chloride. When a liquid air bath was placed around the tube of P, distillation again proceeded normally.

Since complete distillation required a long time, the operation was not carried out to completion every time, but, as soon as sufficient material had been collected, distillation in the reverse direction was started. In this way stannic chloride was distilled backwards and forwards through the silver perchlorate about 25 times. It was noticed that after the fifteenth distillation, the first part of the condensate was yellow or brownish. It appeared, therefore, that a more volatile fraction, consisting of yellow material, had formed. After the distillations were stopped, the second tube of P was cooled in liquid air and kept at that temperature for 14 days. During that period a liquid air bath was periodically placed around the first tube of P to test whether distillation was still proceeding. Even after 14 days traces of condensate could still be observed in the first tube. When distillation was thought

to/...

to be nearly completed, a process of fractionation was begun. The more volatile fraction of coloured material was sealed off first. It was not possible, however, to prevent any uncoloured material from distilling together with the yellow product.

Fractionation was continued until four fractions had been obtained. The remaining volatile material was condensed in the first tube of R and partly fractionated into the second tube before being sealed off as fraction 5. Fraction 6 was the condensate that collected in the remaining bulb of R after having been cooled in liquid air for 23 days without interruption. At no time during the distillations or the fractionations was any volatile crystalline material observed.

After the last fraction had been removed, the whole train, consisting of the units N-M-P, Q-R-S, C-E-F-G and H, was cut up and the various parts were washed with water to remove unreacted silver perchlorate, and with alakli to dissolve any tin compounds. The asbestos column, H, was treated separately. The combined aqueous wash liquids and the alkaline solution were tested for the presence of tin but none was detected. The column, H, which had been removed as a unit, was set vertically, and solvents were passed down it under suction to extract the several

substances/...

substances present. The first solvent used was water, to extract unreacted silver perchlorate and to hydrolyse any tin compound. Although no water-soluble silver was found, the water extract contained a small amount of perchlorate. The next solvent that was used was aqueous ammonia, to dissolve out silver chloride. This extract was acidified with chloride-free nitric acid to precipitate the dissolved silver chloride and the residual solution was analysed for tin, chloride and perchlorate. The perchlorate content was found by repeatedly evaporating aliquot parts of the solution with hydrochloric acid to remove nitrate, precipitating most of the chloride with silver sulphate and determining the perchlorate colorimetrically by the methylene blue method[92]. The asbestos column was then eluted several times with aqueous chloride-free sodium hydroxide and finally with concentrated hydrochloric acid. The last two elutions and the residue on the column contained no silver.

(c) Results.

The results of the analyses of the volatile fractions and of the various wash liquids used on the asbestos column are given in table 11. The percentage recovery of tin, chloride and perchlorate were calculated as before.

The/...

Table 11

Analysis of fractions from heterogeneous reaction

Fraction No.	Sn milli-moles	Cl milli-moles	ClO_4 milli-moles	Ratio Sn:Cl:ClO_4	Corrected Ratio ClO_4/Sn
1	0.0042	0.0105	0.0060	1:2.50:1.43	3.75
2	3.313	13.05	nil	1:3.94: -	-
3	5.481	21.93	nil	1:4.00: -	-
4	3.340	13.28	nil	1:3.98: -	-
5	0.4312	1.032	0.6901	1:2.39:1.60	3.98
6	0.6735	2.388	0.3182	1:3.54:0.47	4.16
$AgClO_4$ plug	-	1.895 (as AgCl)	-	-	-
Water wash	nil	0.0742	0.0921	Ag:Sn:Cl:ClO_4 =	
NH_3 aq. wash	nil	1.257 (as AgCl) 0.0993 (as Cl)	0.0815	1.51:1.00:2.92:2.52	-
NaOH wash	0.3971	1.003	1.924		
HCl wash	0.4366	-	-		
Total recovered	14.08	56.02	3.112		
Total used	15.12	60.48	3.152		
% Recovery	93.1	92.6	98.7		

The/..

The analytical results of the volatile fractions are much the same as those of previous experiments. There appeared to be no difference between the more volatile, yellow fraction and other fractions, so that no explanation for the yellow colour could be made. The exact nature of the material left on the asbestos column was also open to doubt. Although it is clear, from the analytical values, that at least part of the tin was present as its perchlorate, some unreacted stannic chloride and silver perchlorate may have been present as well. The water treatment would then have converted the silver salt to its chloride without leaving any water-soluble silver compound. As a result, only the atomic ratio of the constituents could be calculated. The corresponding "corrected ratio", i.e. the ratio of perchlorate to tin, when allowance had been made for a quantity of tin-equivalent to the total chloride content - being present as stannic chloride, could also not be calculated.

Although this experiment did not produce the expected large yield of stannic perchlorate, the results, together with those of previous experiments, clearly established that stannic perchlorate had been prepared.

SECTION F

ANALYTICAL PROCEDURES

ANALYTICAL PROCEDURES

In the course of the experimental work it was necessary to determine one or more of silver, tin, chloride and perchlorate. Below are discussed the various analytical procedures that were used in this investigation.

The determination of silver.

When the silver content of a sample had to be determined, several standard methods were available, viz. gravimetric determination by precipitation of silver chloride, volumetric determination by Mohr's method[53] or by the Volhard procedure[54] and the sulphide method. Frequently, the silver and perchlorate contents had to be determined in a single sample. When this was the case, the first-mentioned method suffered from the disadvantage that an excess of chloride had to be added, which would have increased the error in the later analysis. This method was thus applicable only to a limited extent.

Whereas volumetric procedures were faster than gravimetric ones, the Mohr titration could be carried out only in neutral solutions. Since frequently the solutions to be analysed had to be either distinctly alkaline or distinctly acid, this method was inapplicable. The Volhard

titration/...

titration, which could be carried out in acid media, was, however, frequently used for the determination of both silver and chloride. For standardisation both 'analar' sodium chloride and constant boiling hydrochloric acid were used as primary standards.

The sulphide method.

When the material under investigation contained silver and tin, both of which had to be determined in a single sample, the sulphide method was used. The sample was made alkaline with sodium hydroxide and saturated with hydrogen sulphide. The silver immediately formed the insoluble sulphide while the tin remained in solution. After the precipitate had been washed with sodium hydroxide to ensure complete removal of the tin, the silver sulphide was treated with nitric acid and heated to fumes several times until no more black particles of silver sulphide could be seen. The solution of silver nitrate was diluted and titrated with thiocyanate.

When the silver was present as silver chloride, concentrated ammonia was used instead of sodium hydroxide. Under these circumstances, however, some tin co-precipitated as the sulphide, but was removed when the precipitate was washed with sodium hydroxide.

Tests/...

Tests, using known weights of silver perchlorate and mixtures of known weights of silver chloride and hydrated crystalline stannic chloride, showed that the recovery of silver ranged from 99.6 to 100.0%.

The determination of tin.

The usual gravimetric procedures for the determination of tin involve precipitation of some tin compound, which is subsequently converted to the oxide by ignition. The precipitated compound may be metastannic acid formed by fuming the solution with nitric acid[55], the cupferron complex, precipitated by the addition of an excess of an aqueous solution of cupferron in the presence of hydrochloric, boric and sulphuric acids[56,57,58], and the hydrated oxide, when precipitated with ammonia at pH4. These methods were found unsuitable, however, for the determination of tin when the chloride and perchlorate contents had to be found in the same sample. On the other hand, the sulphide procedure, in which tin was precipitated as stannic sulphide, was often used since this method enabled both tin and silver to be determined together and the remaining filtrate could be used for further analyses.

The/...

The sulphide method.

When hydrogen sulphide is passed into an alkaline solution of a stannic compound, and the solution is subsequently acidified, stannic sulphide precipitates, and after filtration can be ignited and weighed as stannic oxide. In the absence of other metals of the sulphide group it is not necessary to separate tin by the fluoride procedure. Silver does not interfere.

The main disadvantages of this method were firstly, that the sulphide precipitate was gelatinous, so the washing was difficult, and secondly, that sulphuric acid formed during the ignition. The acid could be removed by the addition of ammonium carbonate and re-igniting to constant weight, but the results were still high. After the residue had been heated to constant weight, the true weight of the stannic oxide could be determined by the method of Caley and Burford[59]. When the residue containing stannic oxide and non-volatile impurities was heated over a moderate flame at about 450°C., with about 15 times its weight of ammonium iodide, and finally ignited to constant weight, the loss of weight due to the removal of stannic iodide corresponded to the weight of pure stannic oxide in the original residue.

The complete method outlined above, including the ammonium iodide treatment, was tried on various solutions

of/...

of tin made by dissolving wire in hydrochloric acid. The results of these tests showed that the recovery of tin amounted to 99.7 to 100.0%.

Since the stannic sulphide was precipitated in a gelatinous form, it required many washes with dilute acid solutions. The first few washes were carried out by decantation, while later washes were made directly on the filter paper. The tedium of this method was balanced by the fact that none of the compounds added interfered with analyses that had to be carried out on the filtrate. The presence of chloride did not affect the results of the tin content and the filtrate, after having been boiled to expel hydrogen sulphide, could be used for chloride or perchlorate analyses when these were required.

When both silver and tin had to be determined in a single sample, the same procedure could be used for both metals. After the solution had been made alkaline with sodium hydroxide, which had to be free from chloride if chloride analyses were to be carried out on the filtrate, and saturated with hydrogen sulphide, the silver sulphide was filtered off. On acidifying the filtrate with sulphuric acid, the stannic sulphide precipitated.

The procedure, which had already been tested for determining silver and tin individually, was tested on

samples/...

samples containing both metals. The results of these tests are given in table 12. Samples 1, 2 and 3, prepared by dissolving a known weight of silver chloride in ammonia and adding to it a known weight of anhydrous stannic chloride, were analysed for silver and tin. Samples 4, 5 and 6 were prepared by dissolving a known weight of stannic chloride in chloride-free sodium hydroxide and adding to it a solution of a known weight of silver chloride in ammonia. On mixing the solutions, a black precipitate of silver oxide formed, but this was not filtered off. Analyses of silver, tin and chloride were carried out on these samples. Samples 7 to 10 were prepared by mixing a sodium hydroxide solution of a known weight of stannic chloride with an aqueous solution of a known weight of silver perchlorate. The precipitate which formed when these two solutions were mixed was not filtered off. The samples were analysed for silver, tin, chloride and perchlorate. The results of these tests showed that the method was suitable for the determination of tin and silver even when the chloride and perchlorate contents also had to be found.

Table 12/...

TABLE 12

Complete test of sulphide procedure

No.	Weight used				Weight recovered				% Recovery			
	Ag g.	Sn g.	Cl g.	ClO_4 g.	Ag g.	Sn g.	Cl g.	ClO_4 g.	Ag	Sn	Cl	ClO_4
1	0.0915	.1024	.1524	-	.0911	.1020	.1527	-	99.5	99.6	100.2	-
2	.0787	.1081	.2550	-	.0786	.1075	.2560	-	99.9	99.5	100.4	-
3	.1183	.1430	.2098	-	.1180	.1426	.2101	-	99.7	99.7	100.1	-
4	.1216	.2124	.2938	-	.1211	.2116	.2937	-	99.6	99.6	100.0	-
5	.1108	.1639	.2320	-	.1107	.1628	.2323	-	99.9	99.3	100.1	-
6	.1002	.1308	.1892	-	.0998	.1306	.1892	-	99.6	99.9	100.0	-
7	.0983	.1109	.1323	.0905	.0980	.1111	.1323	.0901	99.7	100.2	100.0	99.6
8	.1048	.0908	.1085	.0966	.1049	.0902	.1087	.0966	100.1	99.3	100.2	100.0
9	.1007	.1085	.1295	.0926	.1006	.1084	.1297	.0922	99.9	99.9	100.2	99.6
10	.1073	.1218	.1455	.0988	.1066	.1214	.1451	.0986	99.3	99.7	99.7	99.8

Volumetric methods.

The volumetric determination of tin depends on the reduction of stannic to stannous tin and re-oxidation with a standard oxidising solution.

Evans[60] described an apparatus which could be used for the reduction of stannic solutions. Using this apparatus, it was possible to reduce the tin solution with nickel and hydrochloric acid, according to the procedure given by Evans and Higgs[61]. It was found, however, that the greenish colour imparted to the solution by the nickel made the exact endpoint of the titration uncertain.

Frankel[62] recommended the use of aluminium and hydrochloric acid as reducing agent, without the necessity of using the Evans apparatus, but all the fragments of metal had to be dissolved before the titration. An atmosphere of carbon dioxide was maintained throughout the titration by dropping a few pieces of marble into the acid solution.

The volumetric procedure has the advantage of speed, but since the presence of hydrochloric acid seriously affected the chloride and perchlorate analyses, the method was infrequently used.

The/...

The polarographic method.

Lingane[66,67] recommends the use of normal hydrochloric acid containing 4N ammonium chloride as the supporting electrolyte for tin determinations. Under these conditions two waves are obtained with half-wave potentials of -0.25 and -0.52 volts respectively. The use of the second wave is recommended for analytical purposes.

Small quantities of stannic tin can be determined polarographically in strong acid solutions which contain a large concentration of chloride[63]. In sulphuric or nitric acid the tin is hydrolysed and precipitates, while no reduction wave was detected in perchloric acid[64]. If, however, sodium chloride is added to the latter, a reduction wave with a half-wave potential of -0.47 volts relative to the standard calomel electrode is obtained[65]. This wave can be used for the quantitative determination of tin.

The method that was used for the determination of small amounts of tin was that recommended by von Stackelberg[65]. The supporting electrolyte consisted of a 2N solution of perchloric acid containing 0.5N sodium chloride. The apparatus was an Heyrovsky-type polarograph and polarograms were photographically recorded on photosensitive paper.

The/...

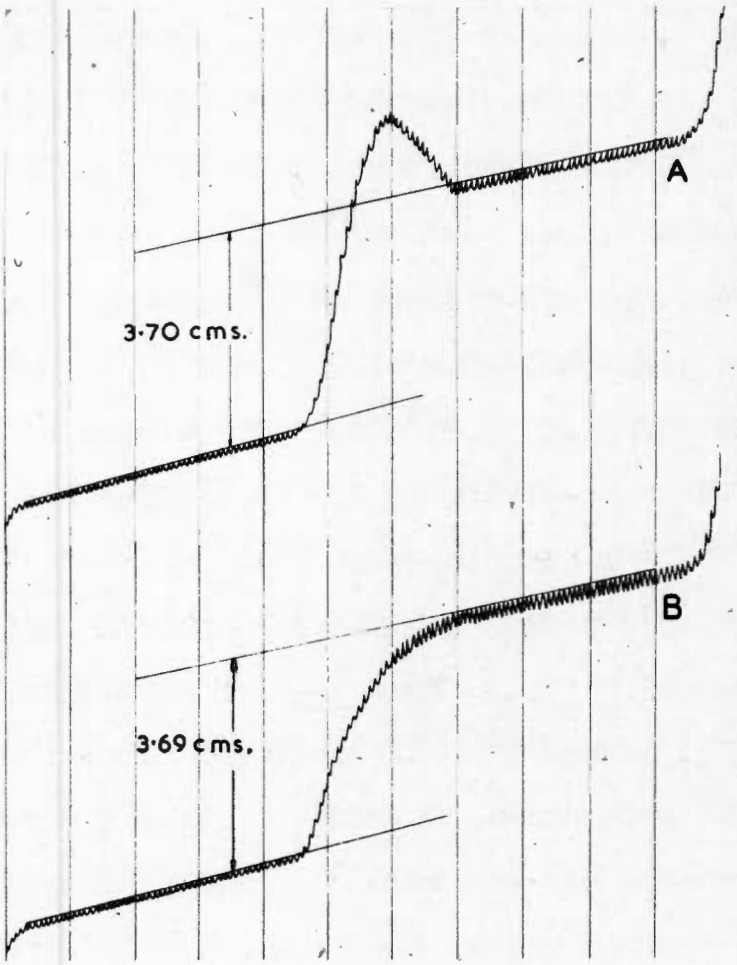


FIGURE 16

The method was tested by using a standard tin solution in 2N perchloric acid and 0.5N sodium chloride. It was found that the polarogram showed a sharp maximum, which was undesirable. As the addition of certain dyes suppresses polarographic maxima, the action of nigrosine was tried. The addition of 1 ml. 1% aqueous nigrosine to 250 ml. of the tin solution completely suppressed the maximum, without changing the height of the step, measured with an accuracy of 0.01 cm. Figure 16 shows the effect of nigrosine.

The reliability of the procedure was tested by obtaining polarograms of various diluted solutions. The results of this test are given in table 13 and it can clearly be seen that the height of the step was directly proportional to the concentration of tin.

Table 13

Polarographic determination of diluted tin solution

Concentration C Molarity	Height of Step h (cm.)	$\frac{C}{C_o}$	$\frac{h}{h_o}$
5.80×10^{-3} (C_o)	3.70 (h_o)	1.0	1.0
2.90×10^{-3}	1.85	0.500	0.500
1.45×10^{-3}	0.93	0.250	0.251
1.16×10^{-3}	0.75	0.200	0.203
7.25×10^{-4}	0.46	0.125	0.124

It/...

It was found that the polarograph could be used for concentrations of tin as low as 10^{-5} molar with an accuracy of about 2%. This compared very favourably with other micro analyses.

Determination of chloride.

The determination of chloride either by volumetric or gravimetric methods presented no difficulties. Under various conditions, the appropriate standard procedures could be applied. For the determination of micro quantities the microdiffusion technique was used.

Microdiffusion.

Conway(69) determined chlorides by oxidation to chlorine gas and by absorbing the gas in concentrated aqueous potassium iodide. The iodine which is liberated can be titrated with standard thiosulphate solution using starch as indicator. The recommended procedure for the oxidation is to acidify the measured volume of chloride solution with about 1 ml. 25% sulphuric acid and to add about 1 g. solid potassium permanganate.

The method was tested on standard sodium chloride solutions. It was found that the weight of potassium permanganate was not important as long as an excess was used.

It/...

It was necessary, however, to grind the solid to a fine powder to facilitate its solution in the acidified liquid. 'Analar' sulphuric acid free from chloride, was used, after dilution with distilled water. The potassium iodide absorbent and the starch indicator were freshly prepared solutions made from analytically pure substances.

The chloride solution was measured from a micro-burette into the Conway dish which was held at an angle so as to confine the solution to a small part of the outer compartment. Sulphuric acid was added to it but care was taken not to wet the entire glass base. The permanganate was carefully placed on a dry spot in the outer compartment. About 1 ml. 20% potassium iodide was placed in the inner compartment with the aid of a dropper. The edge of the Conway dish and a ground plate were lubricated with a specially prepared grease, made by dissolving paraffin wax in liquid paraffin at 50°C. and cooling the solution to room temperature, in order to close the Conway dish completely. After the lid was in position the dish was carefully rotated so as to dissolve the permanganate. It was essential to avoid spilling any iodide into the outer compartment. The dish was left to stand for 2 hours, after which the iodine was titrated. Two blank determinations were carried out with each batch of samples.

To/...

To account for the solubility of chlorine in the sulphuric acid solution and for the back-diffusion of iodine, the result had to be multiplied by a factor of 1.03[69]. This factor probably included the personal error, and was determined before the method was used. Conway's value of 1.03 was confirmed. All results recorded for the micro-analysis were results that had been corrected by multiplying by this factor.

The determination of perchlorate.

The determination of perchlorate presented serious difficulties since the usual procedures were not applicable. Frequently the analysis had to be carried out in a solution containing a high concentration of sodium sulphate. The presence of this salt introduced large errors in the perchlorate content as found by precipitation of potassium perchlorate and nitron perchlorate[71,72]. Reduction with ammonium chloride[70] also led to high results. When, however, reduction was effected by titanous sulphate[81] excellent results were obtained.

Small quantities of perchlorate could be determined colorimetrically with methylene blue[92]. As this dye forms an insoluble precipitate with perchlorates, the decrease of absorption of light at 6084 Å, the wave-length

of/...

of maximum absorption of methylene blue, could be related to the concentration. At pH 2.5 it was found that results could be reproduced with an accuracy of 2%.

Reduction with titanous sulphate[81].

In the presence of sulphuric acid, titanous salts quantitatively reduce perchlorates to chlorides. Use can be made of this reduction to determine the perchlorate content by determining either the chloride formed or the titanous ion that had been used up. Both methods were tried and the former was found to be more convenient.

Pure potassium perchlorate, chloride-free perchloric acid and silver perchlorate were used to investigate this method. The titanous sulphate was made by mixing 100 ml. commercial 15% titanous sulphate, which contained 23% sulphuric acid by weight, with 60 ml. concentrated sulphuric acid and diluting the solution to 350 ml. with freshly boiled distilled water. A known weight of perchlorate was treated with sulphuric acid and about 50 ml., or about double the theoretical amount of titanous sulphate solution. After refluxing in an atmosphere of carbon dioxide for 1 - 2 hours, the excess titanous salt was oxidised and the solution diluted to about 400 ml. with water. Chloride was determined by the Volhard

titration/...

titration. Occasionally it was found that commercial titanous sulphate contained chloride as impurity. When such solutions were used, correction, allowing for this chloride, had to be made.

The concentration of the sulphuric acid during the reduction was an important factor. For complete reduction, a concentration of not less than 13N sulphuric acid was necessary. Under these conditions, reduction was complete after refluxing for about an hour.

A trap containing a solution of sodium hydroxide was connected to the top of the reflux condenser to prevent the loss of any hydrogen chloride or chlorine gas. There was no loss of chloride as long as the titanous was not completely oxidised. After all the titanous salts had been oxidised, the chloride concentration in the trap gradually increased owing to the removal of hydrogen chloride by the current of carbon dioxide. The chloride had therefore to be titrated soon after the removal of the excess titanous salts.

Oxidation of titanous salts could not be carried out with nitric acid or hydrogen peroxide, since these would also oxidise the chloride and result in a low perchlorate value. The best way of removing the titanous sulphate was found to be the addition of an equivalent

amount/...

amount of potassium permanganate. Methyl red was added just before the titanous was completely oxidised, to ensure the minimum loss of chlorine. The smallest excess of permanganate produced chlorine which irreversibly decolorised the methyl red.

Analyses of potassium perchlorate and perchloric acid could be carried out directly on the sample, while in the case of silver perchlorate, it was necessary to remove the silver by boiling with a solution of chloride-free sodium hydroxide before proceeding with the analysis. The addition of relatively large amounts of sodium sulphate did not affect the result.

The alternative procedure, the titration of titanous sulphate, also gave results corresponding to 100% reduction of perchlorate. The titanous solution was standardised with standard ferric ammonium sulphate solution using potassium thiocyanate as an indicator. During the titration the purple colour of the titanous solution gradually faded until, at the endpoint, the formation of red ferric thiocyanate could easily be detected. A known volume of standard titanous sulphate was used for the reduction, after which the excess was back-titrated with ferric ammonium sulphate.

The/...

The disadvantage of the alternative procedure was that the normality of the titanous solution changed appreciably from day to day so that it was necessary to restandardise the solution every time before use.

New micro method for the determination of perchlorates.

The micro determination of perchlorates, other than colorimetric methods, are invariably gravimetric procedures. The absence of a reliable micro balance precluded the use of these methods, so that an attempt was made to adapt the semi-micro volumetric procedure to the micro scale.

In outline, the method consisted of four steps:-

(i) the reduction of perchlorate to chloride with titanous sulphate;

(ii) the oxidation of titanous sulphate with excess potassium permanganate accompanied by the oxidation of the chloride to chlorine;

(iii) the diffusion of chlorine into concentrated potassium iodide solution with the liberation of an equivalent amount of iodine; and,

(iv) the titration of iodine with standard sodium thiosulphate.

The/...

The complete analysis was carried out in a Widmark flask of about 100 c.c. capacity (figure 17). The perchlorate solution was measured into the flask and washed down with freshly boiled distilled water. A 25% solution of chloride-free sulphuric acid was used to acidify the mixture and after the addition of a measured volume of titanous sulphate solution, the mixture was boiled for about 30 minutes to effect the reduction of perchlorate.

'Analar' potassium permanganate was ground to a fine powder and about 1 g. was weighed into a little glass cup, B. The cup and its contents were gently lowered into the titanous solution. After dropping a 20% potassium iodide solution into the cup or the stopper, A, the stopper was placed in position and tied down with elastic bands. Finally, the flask was tilted to upset cup B containing the permanganate powder.

The mixture was allowed to stand for 2 hours, during which time chlorine diffused into the potassium iodide and liberated iodine. The stopper was removed and the iodine in cup A was titrated directly with sodium thiosulphate using a few drops of starch solution as indicator. During the titration the mixture in cup A was stirred by a slow stream of air bubbles pumped through a fine capillary jet by means of a small centrifugal pump.

With/...

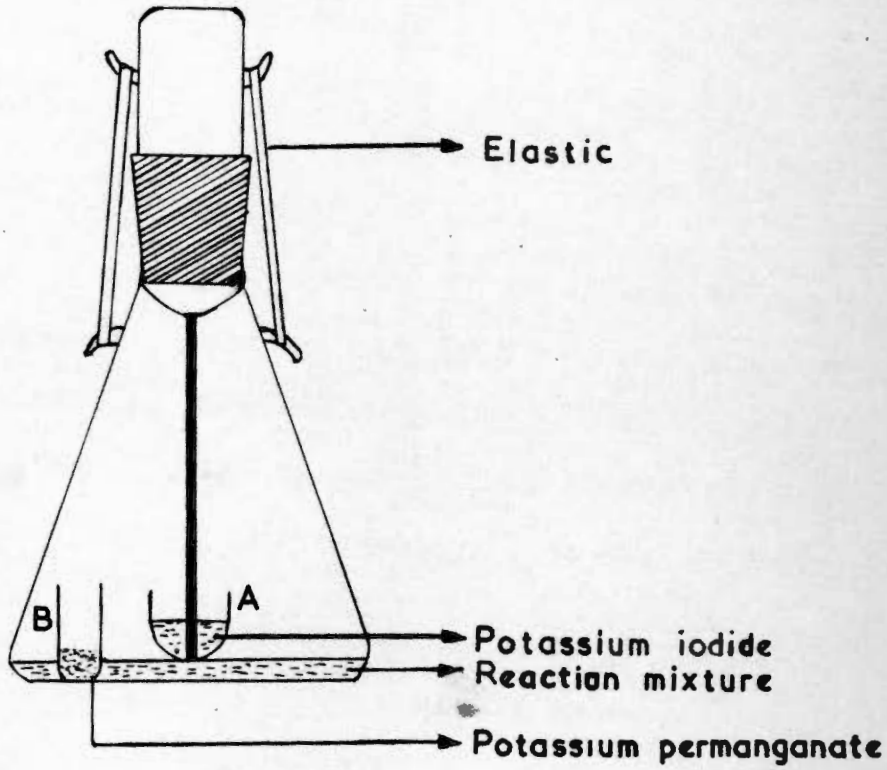

Elastic
A
B
Potassium iodide
Reaction mixture
Potassium permanganate

FIGURE 17

With each determination a blank was carried out with the same quantities of reagents, but with the perchlorate solution replaced by an equal volume of water.

As in the case of the microdiffusion method for the determination of chloride, the results had to be corrected by a factor to obtain the perchlorate content. The determination of this factor showed that while good agreement could be obtained, values of the perchlorate content were occasionally very high or very low, corresponding to very low and very high factors respectively. Some of the results of the determination of this factor are given in table 14.

The source of these errors was soon found, but its complete elimination was not possible. When permanganate was added to the titanous solution, the oxidation was accompanied by an evolution of oxygen, which carried a spray of the acid solution into the potassium iodide. This accounted for the very high results. By using a larger cup to contain the permanganate and by tipping the powder in such a way that it lay between the wall of the cup and the wall of the flask, the spray of acid was directed away from the iodide and consequently eliminated that source of error.

The/...

The low results were found to be caused by the evolution of oxygen, which built up a sufficiently high pressure to lift the stopper slightly. The oxygen which blew off carried with it some chlorine. After the pressure had been relieved in this way, the rubber bands pulled the stopper back into position, making it impossible to tell, by inspection, whether the stopper had been opened or not. To eliminate this error, attempts were made to redesign the apparatus to include a trap containing potassium iodide solution through which the oxygen could bubble. The attempts all failed. Modifications in the experimental procedures did not improve matters. An attempt was made to use a stream of nitrogen to carry all the chlorine over into potassium iodide, but this method introduced other serious sources of error.

As a result of the difficulties involved, it was decided to use the microdiffusion method only when no other method could be used. In these cases a relatively large number of analyses were carried out so as to be able to distinguish between the real and apparent perchlorate contents. The results were corrected by the factor (mean value) given in table 14. It is felt that this method of analysis holds considerable promise which would justify further investigation.

Table 14/...

Table 14

Micro determination of perchlorate Determination of factor

Wt. ClO_4 added mg.	Wt. ClO_4 found mg.	% Recovery	Factor	
0.2111	0.1989	94.2	1.06	
0.3292	0.3137	95.3	1.05	
0.3284	0.1117	34.0	2.94 X	Mean
0.3436	0.3232	94.1	1.06	factor
0.3192	0.3105	97.3	1.03	= 1.06
0.3163	0.2927	92.5	1.08	
0.2591	0.2413	93.1	1.07	
0.3361	0.3165	94.2	1.06	
0.3399	0.4906	144.3	0.69 X	
0.3101	0.2925	94.3	1.06	
0.2720	0.2581	94.9	1.05	
0.2801	0.2640	94.2	1.06	

Table 15/...

Table 15

Analysis of silver perchlorate

Method used	Wt. $AgClO_4$ used	Wt. $AgClO_4$ found	% Purity
Gravimetric (as AgCl)	0.1350	0.1343	99.4_9
	0.2684	0.2677	99.7_2
	0.1788	0.1783	99.7_2
	0.2198	0.2190	99.6_3
	0.1174	0.1173	99.9_1
	0.1386	0.1388	100.1
	0.1588	0.1588	100.0
	0.1674	0.1674	100.0
	0.1737	0.1738	100.1
	0.1482	0.1481	99.9_3
Volumetric (by Mohr)	0.1947	0.1946	99.9_5
	0.1838	0.1838	100.0
	0.2013	0.2012	99.9_5
	0.1607	0.1608	100.1

Table 15 (continued)/...

Table 15 (continued)

Method used	Wt. $AgClO_4$ used	Wt. $AgClO_4$ found	% Purity
Volumetric (by Volhard)	0.2025	0.2024	99.9_3
	0.2813	0.2813	100.0
	0.2462	0.2460	99.9_1
	0.3104	0.3103	99.9_5
	0.1976	0.1977	100.0
	0.2184	0.2183	99.9_5
Gravimetric (as $KClO_4$)	0.1114	0.1112	99.8_2
	0.1176	0.1175	99.9_1
	0.1072	0.1071	99.9_1
	0.1205	0.1202	99.7_5
Gravimetric (as nitron perchlorate)	0.0627	0.0638	101.7
	0.0573	0.0576	100.5
	0.0939	0.0940	100.1
	0.1174	0.1177	100.2

Table 16/...

Table 16

Analysis of stannic chloride

Method used	Wt. $SnCl_4$ used	Wt. $SnCl_4$ found	% Purity
Cupferron precipitation	0.2573	0.2572	99.9_6
	0.3368	0.3366	99.9_4
	0.2847	0.2845	99.9_3
	0.3770	0.3766	99.8_9
	0.4008	0.4007	99.9_8
Ammonia precipitation	0.3112	0.3110	99.9_4
	0.3880	0.3880	100.0
	0.3561	0.3558	99.9_2
	0.3375	0.3371	99.9_8
Volumetric (by Volhard) purified sample	0.1541	0.1541	100.0
	0.1037	0.1038	100.1
	0.1118	0.1118	100.0
	0.1475	0.1476	100.0
	0.1266	0.1267	100.1

S U M M A R Y

SUMMARY

Studies of the reaction between silver perchlorate and stannic chloride in the absence of water revealed that the main product was stannic perchlorate. When benzene and ether were used as solvents, side reactions also took place and led to the formation of a complex mixture, the composition of which depended on the relative quantities of silver perchlorate and stannic chloride originally used. A pure sample of stannic perchlorate was isolated when stannic chloride was distilled in vacuo through a plug of solid silver perchlorate.

The investigation of the reaction in benzene showed that, after stannic chloride had been added to a solution of silver perchlorate, the mixture, at the end of the reaction, consisted of three phases, the benzene phase, an immiscible liquid phase, and a solid phase. The immiscible liquid contained the principal products of the reaction and was accordingly more thoroughly studied than the other two phases. It was found that benzene and stannic perchlorate were always present in this liquid, while stannic chloride and free perchloric acid were only found when excess stannic chloride was used. In the presence of excess silver perchlorate this reagent was also found in the liquid phase.

Although/...

Although there were indications that some organic compound formed in the reaction, no such compound could be isolated.

As analytical investigations only succeeded in proving that the immiscible phase was a mixture of compounds, attempts were made to deduce the course of the reaction in benzene by determining the quantities of reagents removed from the benzene phase. These attempts showed that the number of moles of silver perchlorate removed from solution, per mole of stannic chloride (the reaction ratio) varied continuously and depended on the number of moles of silver perchlorate originally mixed per mole of stannic chloride (the initial ratio). The variation was considered to be due to the solution of unreacted reagents in the immiscible liquid layer. It was, however, deduced that both silver perchlorate and stannic chloride were completely removed from solution when these two reagents were originally mixed in the molar ratio of 4 : 1. It was therefore concluded that stannic perchlorate was the main product and the reaction could be represented by the equation

$$SnC_4 + 4AgClO_4 \longrightarrow Sn(ClO_4)_4 + 4AgCl.$$

Certain indications that stannic perchlorate decomposed in the presence of the solvent and excess stannic chloride, were obtained when the reaction in benzene was

studied/...

studied. These indications were corroborated by similar indications in ether when samples, in which the ratio of perchlorate to tin were as high as 32.4 to 1, were isolated by distillation. As a result of these indications it was decided to avoid the use of solvents in the attempt to isolate pure stannic perchlorate.

In the absence of solvents, reaction was effected in vacuo by distilling stannic chloride vapour through a plug of solid silver perchlorate. Reaction took place on the available surface of the solid, and, once this surface had been covered with silver chloride, no further reaction could take place. As a result, the yield of pure stannic perchlorate was very small. The separation of the pure material from a large excess of unreacted stannic chloride was possible, however, by very slow distillation with a small temperature difference between the distillation and the receiver tubes.

Pure stannic perchlorate was found to be a crystalline compound with an appreciable vapour pressure. The crystals formed as long, colourless needles from a solution of stannic perchlorate in stannic chloride when the latter was slowly removed, in vacuo, by distillation. Care had to be exercised in handling pure stannic perchlorate, because of its highly explosive nature. In view of its

high/...

high volatility and explosive nature it was considered likely that stannic perchlorate was a covalent compound.

Since it was essential to work with small amounts of material it was necessary to develop appropriate techniques to analyse such small quantities.

Tin was determined polarographically, while the microdiffusion technique was successfully applied to the determination of chloride. A new method for the micro determination of perchlorate by an indirect titration was developed with partial success. Although certain difficulties in the procedure remain to be solved, the method could be relied upon to give results with an accuracy of better than 2%.

A P P E N D I X

APPENDIX

After the completion of the work described in this thesis, the following note was published by Schmeisser[90].

Investigations with silver perchlorate lead to a series of new reactions. Silver perchlorate reacts with silicon tetrachloride according to the scheme:-

$$SiCl_4 + 4AgClO_4 \longrightarrow Si(ClO_4)_4 + 4AgCl$$

with the formation of a highly explosive volatile liquid, silicon perchlorate, which may be distilled in vacuo at room temperature and which can undergo reactions of the type

$$Si(ClO_4)_4 + 2Mg(Et)_2 \longrightarrow SiEt_4 + 2Mg(ClO_4)_2.$$

This reaction of halide with silver perchlorate is of general application, as was shown by a large number of cases explored. [It may be used] for the preparation of perchlorates of different non-metals, metals or acid halides. It was found that reaction was quantitative and the respective perchlorates formed by the reaction between silver perchlorate and the following chlorides, could readily be separated:-

BCl_3/...

BCl_3	$SiCl_4$	PCl_3	S_2Cl_2	CH_3COCl
$AlCl_3$	$GeCl_4$	$POCl_3$	SCl_2	C_6H_5COCl
	$SnCl_4$		$SOCl_2$	
	$TiCl_4$		SO_2Cl_2	

Although this note refers specifically to the preparation of silicon perchlorate, it may be inferred that the case of stannic perchlorate follows similarly. It is of interest to note that the author found the product to be highly explosive and volatile, which is in agreement with the findings of this thesis. It is to be regretted that Schmeisser did not describe, at least in outline, the methods he used to prepare the perchlorates. It is, however, satisfactory that the properties of stannic perchlorate and its preparation by the reaction between stannic chloride and silver perchlorate as described in this thesis are independently confirmed.

REFERENCES

REFERENCES

(1) Stähler, A. and Wirthwein, H. - Ber., 38, 2619, (1905).

(2) Patscheke, G. and Schaller, W. - Z. anorg. Chem., 235, 262, (1938).

(3) "Gmelins Handbuch der Anorganischen Chemie", No. 41, Titan, Verlag Chemie, Weinheim, (1951) p.348.

(5) Lutschinsky, G.P. - Z. anorg. Chem., 226, 333, (1936).

(6) Glatzel, E. - Ber., 9, 1833, (1876).

(7) Boguslavskaja, B.E. - Zurnal obscej. Chim. (Russ.), 9, 1084, (1939).

(8) Thornton, W.M. - "Titanium", Am. Chem. Soc. Monograph, New York, (1927) p.52.

(9) Blondel, - Bul. soc. chim., Paris, [3], 21, 262, (1899).

(10) Kirkham, A. and Spence, H. - (P. Spence and Sons, Ltd.), B.P., 263,886, (1925).

(11) Roseheim, A. and Schütte, O. - Z. anorg. Chem., 26, 251, (1901).

(12) Weinland, R.F. and Kühl, H. - Z. anorg. Chem., 54, 253, (1907).

(13) Jahr, K.F. and Shin, I. - F.I.A.T. review, Inorg. chem., 3, 171, (1951).

(14) Ruff, O. and Wallstein, R. - Z. anorg. Chem., 128, 96, (1923).

(15)/...

(15) Young, R.C. - J.A.C.S., 53, 2148, (1931).

(16) Fast, J.D. - Z. anorg. Chem., 239, 145, (1938).

(17) von Hevesy, G. and Cremer, E. - Z. anorg. allgem. Chem., 195, 339, (1931).

(18) Remy, H. - "Lehrbuch der Anorganischen Chemie", Akad. Verslag, Leipzig, (1950).

(19) Falinski, M. - Ann. Chim., 16, 237, (1941).

(20) Wedekind, E. and Wilke, H. - Koll. Z., 35, 27, 31, (1924).

(21) Venable, F.P. and Smithey, I.W. - J.A.C.S., 41, 1724, (1919).

(22) von Hevesy, G. and Kimura, K. - Z. angew. Chem., 38, 774, (1925).

(23) Marquis, M., Urbain, P. and Urbain, G. - Compt. rend., 180, 1377, (1925).

(24) von Hevesy, G. and Cremer, E. - Z. anorg. Chem., 195, 340, (1931).

(25) Coster, D. and von Hevesy, G. - B.P., 219,024, (1924).

(26) von Hevesy, G. - Medd. Danske Selsk, 6, No.7, 111, (1925).

(27) Roozeboom, H.W.B. - Z. phys. Chem., 5, 198, (1890).

(28) Rosenheim, A., Samter, V. and Davidsohn, I. - Z. anorg. Chem., 35, 424, (1903).

(29) Wyrouboff, G.N. - Chem. Zent., 494, (1901)i.

(30) Cleve, - Bull. Soc. chim., [ii], 21, 116, (1874).

(31)/...

(31) Birckenbach, L. and Goubeau, J. - Natuurwiss., 18, 530, (1930).

(32) Pugh, W. - J.C.S., 1540, (1929).

(33) Schwarz, R., Schenk, P.W. and Giese, H. - Ber., 64B, 362, (1931).

(34) Østerud, Th. and Prytz, M. - Arch. Math. Naturvidenskab, 47, 107, (1943).

(35) Remy, H. - "Lehrbuch der Anorganischen Chemie", Akad. Verslag, Leipzig, (1950), p.456 et seq.

(36) Ditte, A. - Ann. Chim. Phys., (5), 27, 159, (1882).

(37) Ditte, A. - Compt. Rend., 104, 172, (1887).

(38) Sidgwick, N.V. - "The Chemical Elements and their Compounds", Oxford Univ. Press, (1950), Vol.1, p.611.

(39) Østerud, Th. and Prytz, M. - Arch. Math. Naturvidenskab, 47, 73, (1943).

(40) Denham, H.G. - J.C.S., 115, 111, (1919).

(42) Roth, R. - "Zur Kenntnis der Perchlorate", Dissert. Munich, (1910), p.22.

(43) Marignac, - Jahresber., 398, (1855).

(44) Serullas, - Ann. Chim. Phys., 46, 306, (1831).

(45) Roscoe, - Annalen, 121, 353, (1862).

(46) Brauner, B. - Z. anorg. Chem., 7, 11, (1894).

(47) Friedrich, H. - Ber., 26, 1434, (1893).

(48) Vorländer and van Schilling, - Lieb. Ann., 310, 374, (1900).

(49)/...

(49) Gomberg, M. - J.A.C.S., 45, 403, (1923).

(50) Hill, A.E. - J.A.C.S., 43, 254, (1921).

(51) Hill, A.E. - J.A.C.S., 44, 1163, (1922).

(52) Kabesh, A. and Nyholm, - J.C.S., 3248, (1951).

(53) Mohr, F. - Lieb. Ann., 97, 337, (1856).

(54) Volhard, J. - Lieb. Ann., 190, 1, (1877).

(55) Fresenius, C.R. - "Quantitative Chemical Analysis", 1, (1903) p.403.

(56) Kling, A. and Lassieur, A. - Compt. rend., 170, 1112, (1920).

(57) Furman, N.H. - J. Ind. Eng. Chem., 15, 1071, (1923).

(58) Pinkus, A. and Claessens, J. - Bull. soc. chim. Belge, 31, 413, (1927).

(59) Caley, E.R. and Burford, M.G. - Ind. Eng. Chem., Anal. Ed., 8, 114, (1936).

(60) Evans, B.S. - Analyst, 52, 590, (1927).

(61) Evans, B.S. and Higgs, D.G. - Analyst, 69, 291, (1944).

(62) Frankel, J.J. - J. Chem. Met. Mining Soc. of S. Africa, 39, 290, (1939).

(63) Smrz, J. - Rec. trav. chim. Pays-Bas., 44, 528, (1925).

(64) Kolthoff, I.M. and Lingane, J.J. - "Polarography", Interscience, New York, (1952), p.526.

(65) von Stackelberg, M. - "Polarographische Arbeitsmethoden", De Gruyter, Berlin, (1950) p.131.

(66)/...

(66) Lingane, J.J. - Ind. Eng. Chem., Anal. Ed., 15, 583, (1943).

(67) Lingane, J.J. - J.A.C.S., 67, 919, (1945).

(69) Conway, E.J. - "Microdiffusion Analysis and Volumetric Error", Lockwood, London, (1947) pp. 165 - 176.

(70) Vogel, A.I. - "Textbook of Quantitative Inorganic Analysis", Longman, London, (1951) p.497.

(71) Cope, W.C. and Barab, J. - J.A.C.S., 39, 511, (1917).

(72) Flagg, J.F. - "Chemical Analysis. Organic Reagents", Interscience, New York, (1948), 4, p.242.

(73) Menon, A.S. - Kolloid - Z., 78, 272, (1937).

(74) Mecklenburgh, W. - Z. anorg. Chem., 64, 368, (1909).

(75) Mecklenburgh, W. - Z. anorg. Chem., 74, 207, (1912).

(76) Mecklenburgh, W. - Z. anorg. Chem., 84, 121, (1913).

(77) Ardagh, E.G.R. and Furber, C.M. - J.S.C.I., 48, 73T, (1929).

(78) Birckenbach, L. and Goubeau, J. - Ber., 64B, 218, (1931).

(79) Kuhlmann, F. - Ann. Chim. Phys., (3), 2, 118, (1841).

(80) Lewy, B. - Ann. Chim. Phys., (3), 16, 303, (1846).

(81) Rothmund, V. - Z. anorg. Chem., 62, 109, (1909).

(82) Weiser, H.B. and Milligan, W.O. - Chem. Rev., 25, 1 - 30 (1939).

(84) Shrader, S.A. and Ritzer, J.E. - Ind. Eng. Chem., Anal. Ed., 11, 54, (1939).

(85)/...

(85) Mazzuchelli, A. and Vercillo, - Gazz., 55, 498, (1925).

(86) Mazzuchelli, A. and Pro, D. - Gaz., 56, 111, (1926).

(87) Van Wyk, - Z. anorg. Chem., 48, 42, 45, (1906).

(88) Biron, E.V. - J. Russ. Phys.-Chem. Soc., 42, 135, (1910).

(89) Young, S. - Proc. Roy. Dublin Soc., 12, 374, (1910).

(90) Schmeisser, M. - Angew. Chem., 65, 324, (1953).

(91) Bruce, J., Challenger, F., Gibson, H.B. and Allenby, W.E. - J. Inst. Petroleum, 34, 226 - 235, (1948).

(92) Snell, F.D. and Snell, C.T. - "Colorimetric methods of analysis", Vol.III, 3rd Ed., New York, (1949), pp. 718 - 719.